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CHEMISTRY

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ADSORPTION

UDC 541.135.5-183:547

EFFECT OF SOLVENT ON FORM OF DIFFERENTIAL CAPACITY CURVES IN ADSORPTION OF TETRABUTYLAMMONIUM CATIONS

Moscow ELEKTROKIMIYA in Russian Vol 18, No 12, Dec 82
(manuscript received 1 Dec 81) pp 1674-1677

KARPOV, S. I. and DAMASKIN, B. B., Moscow State University
imeni M. V. Lomonosov

[Abstract] In studying the title adsorption, in aqueous solution a characteristic slanting maximum was discovered before the cathode peak of adsorption-desorption. Study on a mercury electrode in anhydrous solvents such as ethanol and ethylene glycol showed no such slanting maximum. Other experimental data showed that in the transition from an aqueous to an anhydrous solution cation deformation was hampered, and did not take place in anhydrous solutions at all. Other data show the relationship between the diffusion layer and TBA salts. The authors present calculations to show that as water is replaced by a solvent with a lower density, the slanting maximum, typical for aqueous solutions, gradually disappears from differential capacity curves. Figures 3; references 9 (Russian).

[108-12131]

UDC 541.135.52:546.98

STUDY OF ADSORPTION AND ELECTROCHEMICAL PROPERTIES OF THIN PALLADIUM FILMS ON NICKEL

Moscow ELEKTROKIMIYA in Russian Vol 18, No 12, Dec 82
(manuscript received 3 Dec 81) pp 1678-1680

RIVERA GARCIA, A. E., SKUNDIN, A. M., KONDRASHEVA, V. S. and
GRYAZNOV, V. M., Friendship of Peoples University imeni Patrice Lumumba,
Moscow; Institute of Electrochemistry, USSR Academy of Sciences, Moscow

[Abstract] Palladium and its alloys as membrane catalysts penetrable only by hydrogen are finding numerous industrial applications, but even thinner

coatings are desirable in some uses. The authors studied palladium coatings deposited by chemical precipitation on nickel at 50°C and measured adsorption of hydrogen and oxygen, emission of hydrogen and methanol oxidation. Surface area of the palladium was measured on the basis of earlier studies that showed that desorption of oxygen from a palladium block was the same as from a thin palladium layer on a carbon base. In a solution of sulfuric acid, it was found that the oxygen desorption and adsorption and emission of hydrogen from samples of uncoated nickel was insignificant compared to that when even incomplete coatings of palladium had been deposited. Where a coating of palladium had been applied in 1 minute and had an effective thickness of about 70 nm, the flow density of hydrogen was only about half that from solid palladium, but otherwise, the palladium coating applied in ca. 15 minutes provided the same hydrogen flow as a solid palladium sample.

Figures 2; references 5: 4 Russian, 1 Western.

[108-12131]

ALKALOIDS

UDC 547.944/945

ALKALOIDS OF NITRARIA KOMAROVII, PART 5: STRUCTURE AND SYNTHESIS OF KOMAROVYCIN

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, Sep-Oct 82
(manuscript received 26 Oct 81) pp 633-635

TULYAGANOV, T. S., IBRAGIMOV, A. A. and YUNUSOV, S. Yu., Order of Labor
Red Banner Institute of Plant Substance Chemistry, UzSSR Academy of
Sciences, Tashkent

[Abstract] Continuing previous research of alkaloids of *Nitraria komarovii* Iljin et Lava (this journal, 1980, p 732, 1981, p 192), the authors isolated a substance with melting point of 209-210° C (CH_2Cl_2) with a composition of $\text{C}_{20}\text{H}_{17}\text{N}_3$ and named it komarovycin. Its structure was examined by infrared, PMR and mass spectroscopy which determined that it differed from previously identified "komarovin" by the presence of 4 hydrogen atoms. They suggest its structure to be 3,4,5,6-tetrahydro-3-(8'-quinolyl)-beta-carboline. Laboratory synthesis showed this structure to be accurate. Chemical and spectrographic procedures are summarized in the experimental section. References 4 (Russian).
[107-12131]

UDC 547.944/945

ALKALOIDS OF NITRARIA KOMAROVII, PART 6: STRUCTURE AND SYNTHESIS OF ISOKOMAROVIN AND KOMAROVIDININE

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, Sep-Oct 82
(manuscript received 26 Oct 81) pp 635-638

TULYAGANOV, T. S., IBRAGIMOV, A. A. and YUNUSOV, S. Yu., Order of Labor
Red Banner Institute of Plant Substance Chemistry, UzSSR Academy of
Sciences, Tashkent

[Abstract] Continuing previous study of *Nitraria komarovii* Iljin et Lava alkaloids, (this journal, 1981, p 192), the authors divided esters of plants

harvested in August 1979 according to solubility, and isolated two bases with chromatography using silicagel in a column. The base with melting temperature of 321-322° C (CH_2Cl_2) and composition of $\text{C}_{20}\text{H}_{13}\text{N}_3$ they named isokomarovin; the other, with M.P. of 254-255° C and composition of $\text{C}_{20}\text{H}_{11}\text{N}_3$ they named komarovidinine. Ultraviolet and PMR spectra helped to establish the structure of the former as 9H-pyrido-[3,4-b]indolo,1-(5-quinolinyl), and of the latter as indolo[3,2,1,-de]quinolino[4,5,gh][1,5]naphthiridine. Chemical procedures and spectrography are summarized in the experimental section. References 5: 4 Russian, 1 Western.
[107-12131]

UDC 547.944/945

ALKALOIDS OF NITRARIA KOMAROVII, PART 7: STRUCTURE AND SYNTHESIS OF KOMAROVININE

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, Sep-Oct 82
(manuscript received 26 Oct 81) pp 638-640

TULYAGANOV, T. S., IBRAGIMOV, A. A. and YUNUSOV, S. Yu., Order of Labor Red Banner Institute of Plant Substance Chemistry, UzSSR Academy of Sciences, Tashkent

[Abstract] Continuing their previous research (this journal, 1981, p 192), the authors used column chromatography of the esters to isolate a new crystalline, optically inactive base with melting point of 239-240° C and composition of $\text{C}_{20}\text{H}_{13}\text{N}_3$, which they named komarovinine. Mass, ultraviolet, infrared and PMR spectra indicated its complete aromatic nature and its structure, 3-(6'-quinolyl)-beta-carboline. This composition was confirmed through synthesis of identical compounds. Chemical procedures and spectral findings are summarized in the experimental section. References 5: 4 Russian, 1 Western.
[107-12131]

UDC 547.944/945

SUBHIRZINE, NEW ALKALOID OF CONVULVULUS SUBHIRSUTUS ROOTS

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, Sep-Oct 82
(manuscript received 30 Oct 81) pp 640-642

ARIPOVA, S. F., SHAROVA, Ye. G. and YUNUSOV, S. Yu., Order of Labor Red Banner Institute of Plant Substance Chemistry, UzSSR Academy of Sciences, Tashkent

[Abstract] Previous study of the title plant roots gathered in the vicinity of the village of Dzhilg, Chimbentskaya Oblast, KazSSR during rapid growth

periods, had led to isolation of 5 alkaloids: convolvine, convolamine, fillalbin, convolidine and confoline. The non-phenol part, after separation by a citrate-phosphate solution at pH=6.8 in 10% sulfuric acid, yielded a new fraction. Mass, infrared and NMR spectra, chemical reactions and spectral data of derivatives indicate its structure to be that of a dimer alkaloid of the tropane order. The authors selected the title name. Chemical procedures and spectral data are summarized in the experimental section. References 4: 3 Russian, 1 Western.
[107-12131]

UDC 547.943

ALKALOIDS OF FUMARIA PARVIFLORA

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, Sep-Oct 82
(manuscript received 10 Nov 81) pp 642-644

ALIMOVA, M., ISRAILOV, I. A., YUNUSOV, M. S. and YUNUSOV, S. Yu., Order of Labor Red Banner Institute of Plant Substance Chemistry, UzSSR Academy of Sciences, Tashkent

[Abstract] The title plants were gathered in the region of Ashkhabad during blossoming and early fruit formation. After extraction with methanol, the resulting alcohol was divided into phenol and non-phenol parts and the alkaloids of each part isolated. Further study was made of their alkaloids and bases, resulting in the first identification from this species of the substances chaillantipholine, skulerine, noriuzifine, coclaurine, dihydro-sanguinarine, hydroxosanguinarine, adlumidine, N-methyladlumine and a base. Also isolated and analyzed was previously unidentified d-fumaricine. Chemical procedures are summarized in the experimental section.

References 9: 5 Russian, 4 Western.

[107-12131]

UDC 547.944/945

STRUCTURE OF VALIVINE

Tashkent KHIMIYA PRIRODNYKH SOYEDINENIY in Russian No 5, Sep-Oct 82
(manuscript received 14 Dec 81) pp 644-646

SAMIKOV, K., SHAKIROV, R. and YUNUSOV, S. Yu., Order of Labor Red Banner Institute of Plant Substance Chemistry, UzSSR Academy of Sciences, Tashkent

[Abstract] Continuing separation of the ester and chloroform components of the foliage of *Fritillaria valujevii* Regel (this journal, 1976, p 269), the

authors isolated a new alkaloid using column chromatography with silicagel, with melting point of 256-258° C and composition of $C_{28}H_{47}NO_3$. Mass, infrared and NMR spectra suggest a heterocyclic skeleton of edpethylidine containing two secondary and one tertiary hydroxyl groups. Further discussion of its structure concludes that the tertiary group is positioned on C_{17} . Chemical and spectral data are summarized in the experimental section. References 13: 6 Russian, 7 Western.
[107-12131]

ANALYTICAL CHEMISTRY

UDC 546.799:543/545

LATEST ADVANCES IN ANALYTICAL CHEMISTRY OF TRANSURANIUM ELEMENTS

Leningrad RADIOKHIMIYA in Russian Vol 24, No 6, Nov-Dec 82
(manuscript received 4 Aug 82) pp 700-728

LEBEDEV, I. A. and MYASOYEDOV, B. F.

[Abstract] A general review is presented for the isotopes and their characteristics of the transuranium elements (TUE) Am, Cm, Pu, Bk, Cf, Fm, Es, Md, Np and Lr and their properties as metals, oxides, and aqueous solutions. Special consideration is given to the following topics: Methods (especially extractions) for separating the TUE's into radiochemically pure form; radiochemical methods (especially emission spectroscopy) for measuring TUE's; X-ray and X-ray fluorescence techniques; mass spectroscopic determination of the isotopic composition of the TUE's; neutron activation analysis of Np and Bk; spectral emission analysis of Am and Cm; luminescence analysis of Np; calorimetric analysis of Pu; electrochemical (polarographic) methods, especially for Am, Cm, Pu and Np; and titration and spectrophotometric methods. Special problems in measuring traces of non-radioactive contaminants in radionuclide material are mentioned. Tables 6; references 307: 151 Russian, 156 Western.
[124-12027]

UDC 615.31:547.564.4]074:543.253

INDIRECT POLAROGRAPHIC DETERMINATION OF PARACETAMOL

Moscow FARMATSIYA in Russian Vol 31, No 6, Nov-Dec 82
(manuscript received 5 Nov 81) pp 42-45

BEZUGLYY, V. D., ZHUKOVA, T. V., SHAPOVALOV, V. A. and SLYUSAR', S. N.,
Kharkov Pharmaceutical Institute

[Abstract] Wide use of polarography for analysis in preliminary chemical reactions makes it possible among other things to measure primary amines and,

indirectly, to analyze amides through acid hydrolysis. The authors used various aldehydes, benzaldehyde and its derivatives and formaldehyde and determined the optimal pH to be 2.1 for azomethine formation. Hydrolysis completion was evaluated through the reaction of amine condensation with formaldehyde and polarographic comparison of Schiff-base wave peaks obtained from pure para-aminophenol and the hydrolyzate. Results indicated that hydrolysis did not proceed to its conclusion, but to a state of balance. Control tests with medications such as caffeine, amidopyrine, sodium caffeine-benzoate and ascorbic acid showed that under the selected conditions these components had no effect on reduction of the corresponding Schiff base or the results of analysis. The procedure was found suitable and effective for determining paracetamol content in tablets, capsules and powders with relative error of 2-5%. Figure 1; references 5 (Russian).
[101-12131]

UDC 546.185:546.273

BOROPHOSPHATE CATALYSTS

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA, SERIYA 2: KHIMIYA in Russian Vol 23, No 6, Nov-Dec 82 (manuscript received 15 Jun 82) pp 543-554

KUBASOV, A. A., Department of Physical Chemistry, Moscow State University
Imeni M. V. Lomonosov

[Abstract] This is a review of catalyst advances including the search for new, complex systems and perfection of known systems. Reactions involving both acid and base aspects with boron, phosphorus and hydrogen in compounds such as $B-OH-P$ and BPO_4 are discussed in terms of stoichiometry, structure and durability. The author and his collaborators studied borophosphates to determine their activity in cyclohexane conversion and dehydration of *n*-butyl alcohol. The compounds B_2O_3 and P_2O_5 could not be studied in the presence of water due to their high solubility. The crystalline phase had a cristobalite structure when obtained at 400°C and above. With a ratio of P:B of 1, catalysts were obtained with either proton donor or Lewis acidity features, but the method was uncertain and further development was attempted to make it more dependable. Methods involving the reaction of orthophosphoric acid and ethyl or butyl ester of boric acid, and a variant "cryochemical" synthesis, were tested. Results indicated that the best activity of borophosphates came with regular structure, acidity of +3.3 to +5.5 with coordinated selective Lewis and Brandstad reactions. Further tests sought to determine activity in ethylene hydration to obtain a water-alcohol condensate, determine activity in ethylene hydration to obtain a water-alcohol condensate, determine the simplest carrier, (which turned out to be diatomite and silicagel) and improve stability by introduction of additional silicon. References 33 (Russian).
[126-12131]

EFFECT OF VARIABLE CURRENT PROCESSING IN H_3PO_4 SOLUTIONS ON SURFACE
PROPERTIES OF TITANIUM ALLOYS

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 48, No 12, Dec 82
(manuscript received 8 Feb 82) pp 1264-1267

DMITRUK, B. F., NAZARENKO, N. D. and GRIBKOVA, L. V., Institute of General
and Inorganic Chemistry, UkSSR Academy of Sciences

[Abstract] Previous studies that were devoted to the behavior of titanium alloys in 10-40% solutions of phosphoric acid with polarization by sinusoidal variable currents determined the relationship of surface microhardness to H_3PO_4 concentration and current density (eg., this journal, 1979, pp 68-69, ZHURNAL PRIKLADNOY KHIMII, 1978, pp 184-185). The authors also learned that conditions and electrolysis parameters could be controlled to obtain oxide, oxide-hydride and hydride coatings with varying properties, and another unidentified type of coating of up to 45 mcm with unusual hardness that did not delaminate, crack or fail in other ways, while maintaining its flexible and blow-resistant properties. The present article is devoted to study of that coating. The authors conclude that in the title process the surface hardness of the titanium alloys in a phosphoric acid electrolyte is determined by formation of a solid solution of titanium suboxide (Ti_2O) in the titanium. Specific properties of that suboxide account for the hard, yet flexible and blow-resistant, coating. Figures 3; references 9: 8 Russian, 1 Western. [104-12131]

BIOCHEMISTRY

UDC 663.1

URGENT PROBLEMS IN DEVELOPMENT OF MICROBIOLOGICAL INDUSTRY

Moscow ZHURNAL VSESOUYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D. I. MENDELEYEVA
in Russian Vol 27, No 6, Nov-Dec 82 pp 613-617

RYCHKOV, R. S., chief, Main Administration for the Microbiological Industry

[Abstract] Among the main objectives of the current five-year plan (to 1986) and of the following (to 1991) is the achievement of an increase in scientific and technological advancement specifically in the direction of greater efficiency in industrial processes. This directive applies to microbiology specifically in such areas as contributions to increasing livestock production, for example by improving the quality and effectiveness of fish and meat meal, dry waste products, and other high protein feed additives; providing inexpensive concentrates of vitamins, individual amino acids, enzymes, antibiotics, growth hormones, and other types of specialized complex biochemicals. One new and very promising area is a combination of microelements together with biologically active compounds which facilitate their utilization. In general, this important industry is expected to approximately double by 1986; figures are given for projected increases in some of the major sectors. [125-12027]

UDC 663.14

PROTEIN INDUSTRY

Moscow ZHURNAL VSESOUYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D. I. MENDELEYEVA
in Russian Vol 27, No 6, Nov-Dec 82 pp 617-621

KATRUSH, R. V., candidate of technical sciences, director, All-Union Scientific Research Institute for Protein Synthesis and MIRZAYANOVA, E. G., candidate of chemical sciences, senior scientific associate, All-Union Scientific Research Institute for Protein Synthesis

[Abstract] The increase in protein production to meet the projected requirements for the year 2000 cannot be achieved from traditional sources (meat,

eggs and milk) alone. The strong emphasis on agriculture in the 1981-1985 and 1986-1991 five-year plans also includes emphasis on developing additional sources of protein, both for feed and for primary consumption. Products of microbiological growth are examples of underutilized sources of protein. They have the advantages of rapid production, high relative concentrations of protein, amino acids, vitamins and other essential micronutrients. Petroleum, especially the normal-paraffin component, provides the usual substrate although cultures have been grown on such carbon sources as natural gas, methanol, and ethanol. Economics, particularly when the price of petroleum must be considered, is an important factor. Relative contents of amino acids, B vitamins and other important components are tabulated for biosynthesized protein, fish meal, and soybean flour. References 22: 7 Russian, 15 Western. [125-12027]

UDC 577.1

PROSPECTIVE BIOLOGICALLY ACTIVE COMPOUNDS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D. I. MENDELEYEVA
in Russian Vol 27, No 6, Nov-Dec 82 pp 626-627

OGARKOV, V. I., corresponding member, USSR Academy of Medical Sciences,
deputy chief of the Main Administration for the Microbiological Industry

[Abstract] In 1981, a series of measures was introduced to accelerate development in the areas of molecular biology, bio-organic chemistry, molecular genetics, and genetic engineering. The organism *E. coli* may be used to clone genes for the production of insulin, somatostatin, growth hormones, viral antigens interferon and others. Interferon especially is considered in some detail as an example of the rationale needed to develop micro-organisms capable of producing desired biochemical products. Future developments lie not only in expanding the capabilities of this species but also those of other species such as *Bacillus subtilis* and the yeast *Saccharomyces cerevisiae*. This industry promises to be among the most rapidly-growing segments of the business. It will contribute significantly to the economics of the future and enhance the productivity of many other industries. References 23 (Western). [125-12027]

CURRENT GENETIC SELECTION METHODS FOR OBTAINING INDUSTRIAL MICROORGANISMS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IM. D. I. MENDELEYEVA in Russian Vol 27, No 6, Nov-Dec 82 pp 630-634

DEBABOV, V. G., professor, director, All-Union Scientific Research
Institute of Genetics and Selection of Industrial Microorganisms

[Abstract] The most elementary technique is the selective "breeding" of strains tolerant of specific conditions. It is most applicable to developing organisms to produce primary metabolites such as amino acids. Next most complicated is inducing mutations by physical or chemical means and selecting strains for tolerances or capabilities to produce certain specific biochemicals. The most powerful method of separating mutants is selection based on the stability of the microbe cell to structural analogs of the functional product. The structural analog, when ingested by normal cells, stunts the cell growth; the growth of mutant cells unable to metabolize the structural analog is not hampered. For example, the compound S(2-aminoethyl)cysteine is used as a structural analog of lysine. The most advanced selection technique involves actual genetic engineering. Several types of gene-altering procedures are considered, among them repeating the functional segments in natural gene to increase the yield of a desired product and synthesizing genes to produce products heretofore impractical or impossible to obtain, such as interferon, insulin, hormones and others. Figure 1; references 21: 7 Russian, 14 Western.
[125-12027]

UDC 663.033.002.237

IMPORTANT DIRECTIONS IN IMPROVING BIOCHEMICAL REACTORS

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IM. D. I. MENDELEYEVA in Russian Vol 27, No 6, Nov-Dec 82 pp 640-644

KRYLOV, Yu. V., doctor of technical sciences, manager of Section of
Microbiological Equipment, All-Union Scientific Research Institute of
Biomechanics

[Abstract] Investigations are currently being directed towards improving the purity and yield of existing as well as developing new products, especially in the farming and food industries. The "economy of scale" applicable in many cases cannot be as readily applied as biological media are heterogeneous systems. Models and experimental data must be used to determine the rate of each step in the reaction and to calculate the time necessary to transport the reactants through the reaction zone in a continuous or semi-continuous process. Nutrients and oxygen (for aerobic processes) must be supplied and the undesirable metabolites removed. Keeping

large scale reactors at a proper uniform temperature is difficult; uneven temperatures can cause lowered production or the formation of undesired by-products. Finally, sterilization and sanitation become both more difficult and more important as size increases. Consideration is given specifically to solid-phase fermentation methods.

[125-12027]

UDC 658.562.014

CONTROLLING PRODUCTION QUALITY OF MICROBIOLOGICAL PROCESSES

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IM. D. I. MENDELEYEVA in Russian Vol 27, No 6, Nov-Dec 82 pp 649-652

KARPOV, A. M., candidate of technical sciences, deputy chief of the Technical Administration, Main Microbiological Industry

[Abstract] Quality control must be planned for each stage of the microbiological production cycle. A complex plan for quality control (CPQC) was developed as a basis for standardizing procedures to maximize product quality. In the last five-year plan, the amount of product receiving CPQC certification increased from 25% to 30%. The goal for the current five-year plan is 50% certification. Products which fall under the CPQC program include vitamycin and tilozin (antibiotics for poultry farming), trichodermin (antibiotic for plant protection), voberin, entomophthorin and virus preparations (agents for plant protection), sodium glutamate, crystalline lysine and pure amino acids. The quality of raw protein from cultures and, also, the quantity must increase. Specific steps include not only technological factors such as developing better microbiological strains and optimizing conditions but also management factors such as more efficient utilization of raw materials, better coordination and documentation, and decreased waste.

[125-12027]

UDC 663.033:57.083.138.6

STERILITY IN MICROBIOLOGICAL INDUSTRIES

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IM. D. I. MENDELEYEVA in Russian Vol 27, No 6, Nov-Dec 82 pp 661-665

MATVEYEV, V. Ye., doctor of technical sciences, deputy chief, Main Administration for the Microbiological Industry

[Abstract] Contaminants, particularly in the new large-scale processes for feed protein, amino acids, enzymes, antibiotics and others cause direct loss in quality and decreased yield. The overall effectiveness of sterilization to inhibit or inactivate contaminating, unwanted strains of organisms

is related to the characteristics of the materials and feed streams involved, process parameters such as the rates and volumes of flows, and even to the design of the system, e.g., the number of possible cross-contamination paths and possible areas for liquids to collect. An overall purity P_o of a product can be defined as the product of the purities of each individual step P_y such that $P_o = P_1 \times P_2 \times P_3 \dots$. This is mathematically equivalent to $P_o = P_1^n$ where P_1 is a constant for a given system having n steps. The latter equation is used to calculate actual sterilization conditions necessary for a specific system of purity constant P_1 in order to achieve an acceptable P_o . Conditions are based on the heat resistance of the contaminants, heat transfer of the system, mass, and other physical and engineering parameters.

[125-12027]

UDC 620.9:663.1

ENERGETICS AND INDUSTRIAL MICROBIOLOGY

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IM. D. I. MENDELEYEVA in Russian Vol 27, No 6, Nov-Dec 82 pp 665-669

CHERNOV, G. N., candidate of biological sciences, director of the Group on Retrieval of Technical Information, Microbiological Industry

[Abstract] The energy crisis in the capitalist countries has added impetus to the development of commercial microbiological processes for synthesizing some of the components derived from petroleum and other energy sources. Six products are considered here. 1. Ethanol, which has the potential to replace gasoline as an automotive fuel. Several preparative methods together with energy expenditures are considered. 2. Microbial generation of methane, biogas, on the order of 0.5 to 1.0 m³ gas per kilogram dry weight. 3. Liquid hydrocarbons in the range C-18 to C-24 and glycerides to be obtained by the hydrogenation of algae biomass. About 50% of the algae can be recovered as hydrocarbons. 4. Hydrogen, itself an ideal fuel, obtained from water at present by chemical and electrical methods, which can also be generated by photosynthetic organisms or by cell-less (immobilized) enzyme systems. 5. Preparation of commercial uranium from the intermediate yellow cake using Thiobacillus bacteria. 6. Micro-organism produced protein as beef cattle at one-third the energy expenditure by cattle. Figures are tabulated for projected production of various biologically-derived products, to 1990. References 48: 12 Russian, 36 Western.

[125-12027]

ENZYME COMPLEXES

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA

IM. D. I. MENDELEYEVA in Russian Vol 27, No 6, Nov-Dec 82 pp 673-675

KALUNYANTS, K. A., professor, director of a department at the Moscow Technological Institute for the Food Industry and Consultant to the All-Union Scientific Research Biotechnical Institute

[Abstract] Enzymes will play an increasingly significant role as reaction catalysts because of their high substrate and product specificity and their ability to increase reaction rates by a factor of a million or more. Between 1965 and 1980, the enzyme production for the USSR increased 57 times. For example, the brewing industries use mixtures of amylase, glycoamylase, protease, β -glucanase, hemicellulase and others to break down caramel, polysaccharides and proteins into smaller molecules such as dextrans, peptides and amino acids. Improved strains of organisms such as *Bacillus subtilis* 103 and *Aspergillus foetidus* 26 were developed and introduced into the industry to increase yields and product quality. The complex equipment itself was also improved to increase the utilization of raw materials and decrease the amount of waste and contaminated water. Attempts to use an immobilized enzyme mixture called amylsubtilin G10Kh containing α -amylase, protease, β -glucanase and hemicellulase resulted in the partial breakdown of the reactants: caramel to dextrans and proteins to polypeptides. Further development of such solid enzyme systems is one of the goals for the second phase of development of enzyme complexes. References 4 (Russian). [125-12027]

UDC 615.35.015.4

CLASSIFICATION OF CHEMICAL COMPOUNDS BY SPECTRUM OF BIOLOGICAL ACTIVITY,
PART 1: METHODOLOGY

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 17, No 1, Jan 83
(manuscript received 9 Jun 82) pp 63-66

ORDUKHANYAN, A. A., SARKISYAN, A. S., LANDAU, M. A., MNDZHOYAN, Sh. L. and TER-ZAKHARYAN, Yu. Z., Institute of Fine Organic Chemistry, ArSSR Academy of Sciences, Yerevan; Scientific Research Institute of Biological Testing of Chemical Compounds, Moscow Oblast

[Abstract] Evaluation of biologically active compounds is a multiparameter task, usually complicated by varying characteristics of the properties being evaluated. Obviously, description of a single biological property cannot represent the total biological activity of a compound. Therefore, biological effects are described by a spectrum of activities. So far very few publications

have appeared in the area of structure-activity relationships in which not only the primary effect but also the side effects were analyzed. In the present study, a novel approach was taken based on the theory of pattern recognition methods, using cluster analysis approach. It has been proposed to use a method of identification of chemical compounds based on their biological activity spectrum, according to which any compound could be identified as a member of a particular class of active compounds. References 17: 11 Russian (4 by Western authors), 6 Western.
[152-7813]

UDC 615.334.015.11

CLASSIFICATION OF CHEMICAL COMPOUNDS BY SPECTRUM OF BIOLOGICAL ACTIVITY,
PART 2: ALKOXYPHENYLCYCLOALKYLPENICILLINS

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 17, No 1, Jan 83
(manuscript received 9 Jun 82) pp 66-71

ORDUKHANYAN, A. A., SARKISYAN, A. S., LANDAU, M. A., MAGAKYAN, A. R.,
MNDZHOYAN, Sh. L. and TER-ZAKHARYAN, Yu. Z., Institute of Fine Organic
Chemistry, ArSSR Academy of Sciences, Yerevan; Scientific Research
Institute of Biological Aspects of Chemical Compounds, Moscow Oblast

[Abstract] The classification method developed in the preceding paper was used in an analysis of biological activity of alkoxyphenylcycloalkylpenicillins. Five types of biological activity were tested: antibacterial, sensitivity to penicillinase from Staph. and Licheniformis, acid resistance and toxicity. A hierarchical tree of clustering was developed for some 52 derivatives. Cluster analysis was performed and four classes of compounds were identified differing statistically and objectively in their biological properties. Projections of the starting 52 derivatives in the varimax-factor plane and the first two canonic variables illustrated distribution of these compounds in the sphere of biological parameters. Figures 3;
references: 4 Russian.
[152-7813]

UDC 615.015.11

ONE EVALUATION CRITERION FOR HANSCH'S MODEL RELIABILITY

Moscow KHIMIKO-FARMATSEVTICHESKIY ZHURNAL in Russian Vol 17, No 1, Jan 83
(manuscript received 19 Jan 83) pp 71-73

FRUMIN, G. T. and CHURNOSOV, Ye. V., Military Medical Academy
imeni S. M. Kirov, Leningrad

[Abstract] To evaluate statistical reliability of Hansch's model by r^2 (square of correlation coefficient), one needs to determine r_r^2 -- obtained

from an experimental data set--and compare it with r_{cr}^2 (critical value of the square of multiple correlation coefficient) obtained from the formula $r_{cr}^2 = 1.5137 - 0.3697 q + 0.0290 q^2$. If $r_r^2 > r_{cr}^2$ then the model is statistically significant, because its r_r^2 value, resulting from its content along with the experimental "noise", exceeds the value r_{cr}^2 which is due to the "noise" alone. In principle, this approach can be taken with other models, beyond that developed by Hansch. References 9: 6 Russian, 3 Western.
[152-7813]

UDC 577,391:576,3

EXCESS SYNTHESIS OF DNA IN HELA CELLS AFTER γ -IRRADIATION AND TREATMENT WITH N-METHYL-N'-NITRO-N-NITROSOGUANIDINE

Moscow DOKLADY AKADEMII NAUK SSSR in Russian Vol 268, No 3, Jan 83
(manuscript received 30 Jun 82) pp 739-742

BELOSTOTSKAYA, G. B. and MALINOVSKIY, O. V., Leningrad Institute of Nuclear Physics, USSR Academy of Sciences, Gatchina, Leningrad Oblast

[Abstract] Working with a flow-through laser cytofluorometer, cells were identified with excessive content of DNA. This phenomenon was analyzed by two independent experiments on Hela cells subjected to γ -irradiation and exposed to N-methyl-N'-nitro-N-nitrosoguanidine. The results showed that the control cell population had an almost doubled content of DNA, while the cells treated with DNA damaging agents had levels exceeding this doubling of DNA. This oversynthesis was observed in all experimental cases; it was directly related to the dose of the damaging agent. If this oversynthesis really does take place, an excessive pick-up of radiolabelled thymidine should have been noted. In experiments designed to limit radioactivity pickup to only the first replication cycle, it was shown that excessive radioactivity was indeed picked up in all cases exposed to the damaging actions; with the alkylating agent the radioactivity pickup exceeded the oversynthesis of DNA. This led to a conclusion that radioactive thymidine registers not only replications, but also reparative synthesis of cells. Figure 1; references 14: 4 Russian, 10 Western.
[150-7813]

CATALYSIS

UDC [661.257:66.097.3].002.237

PRODUCTION STUDIES OF NEW CATALYSTS FOR SULFURIC ACID INDUSTRY

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 1, Jan 83 pp 32-34

MASLENNIKOV, B. M. and ILLARIONOV, V. V.

[Abstract] Intensive growth of sulfuric acid production has placed new requirements on the catalysts used in various processes. The present paper is a review type survey of the studies of catalytic material. Production of new catalysts is discussed with higher stability at elevated temperatures, optimal porosity, lowered hydraulic resistance and low ignition temperature (below 370°C). These novel catalysts led to development of advanced reaction conditions, making it possible to work under high pressure at elevated concentrations of SO₂. A number of specific examples of individual catalysts is reported. Figures 2; references 16: 14 Russian, 2 Western.
[153-7813]

UDC 546.001:54-36+549.52

BASIC APPROACHES TO DEVELOPING THEORY OF CATALYST PREPARATION; CRYSTALLIZATION BY ORIENTATION ACCRETION METHOD: ESSENCE OF THE PROBLEM

Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKIKH NAUK in Russian No 6, Nov 82 pp 28-35

BUYANOV, R. A. and KRIVORUCHKO, O. P., Institute of Catalysis, Siberian Division, USSR Academy of Sciences, Novosibirsk

[Abstract] Recent recognition of the complexity of multi-component catalysts (containing oxides, salts and metals, for example) have led to efforts to identify the structural and dynamic parameters of all phases and their interaction. The authors studied the title crystallization at temperatures of 20-100° C, pH of 4-13 and various concentrations of blended solutions. Results indicated that primary particles form a crystalline

structure through reorientation of their polymer structure. This process is discussed in terms of initial nuclei, formation of large secondary crystals, and other features of accretion. Polycondensation is thought to depend on the nature of the anion of the initial salt (such as trivalent aluminum) and the concentration of metal cations. Balance in the various stages of formation of polynuclear hydroxocomplexes came relatively slowly when a significant number of metal atoms were present. Features of polynuclear hydroxocomplexes and a classification of their reactions are given, and structural and kinetic features of secondary particles and the disintegration of primary particle aggregates are summarized. A synchronization effect is observed that involves effects of hydroxides of various metals. Linking of solid phase reactions of hydroxides and their dehydration are shown to be related. References 15 (Russian).

[113-12131]

UDC: 547.313.2:549.67:542.937

CATALYTIC DEHYDROCHLORINATION OF 3,4-DICHLORO-1-BUTENE

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 35, No 11, Nov 82
(manuscript received 6 Aug 81) pp 758-761

CHUKHADZHYAN, G. A., KURGINYAN, K. A., KUKOLEV, V. P., EVOYAN, Z. K. and MELKONYAN, L. N., "Nairit" Scientific Production Union, Yerevan

[Abstract] The possibility was studied of vapor phase catalytic dehydrochlorination of 3,4-DC-1-B, using the salts of various metals applied to active carriers. The catalytic activity of salts of Li, K, Ca, Ba applied to various surfaces was also studied. The catalytic activity of KF depends greatly on the nature of the active surface, with TZKA most active. Reaction temperature also significantly influences the reaction rate, as well as the selectivity of the process. References 2: 1 Russian, 1 Western.

[133-6508]

UDC 541.128

HYDROGENATION OF CROTONALDEHYDE BY TITANIUM DIOXIDE-SUPPORTED RUTHENIUM/PALLADIUM CATALYSTS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 56, No 12, Dec 82
(manuscript received 20 Jan 82) pp 2999-3002

DUKHOVNAYA, T. M., SOKOL'SKIY, D. V. and DZHARDAMALIYEVA, K. K.,
Kazakh State University imeni S. M. Kirov, Alma-Ata

[Abstract] Studies were conducted on the effects of water, 96% ethanol and 0.1 N KOH as solvents for the hydrogenation of crotonaldehyde by 1%

ruthenium/palladium catalysts supported on TiO_2 . Chromatographic analysis of the products of hydrogenation conducted at 20°C showed that in water and ethanol the $\text{C}=\text{C}$ bond is selectively saturated; butyraldehyde appears to be the only product of semihydrogenation. In KOH the products were, in addition to butyraldehyde, butanol, crotonyl alcohol, and an unidentified substance presumed to be a product of croton condensation (polyene). In addition, the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds were nonselectively hydrogenated. Figures 3; references: 6 (Russian).
[129-12172]

CHEMICAL INDUSTRY

UDC 338.45:54+66(1922/81)

INDUSTRIAL CHEMISTRY AND THE USSR SIXTIETH ANNIVERSARY

Moscow ZHURNAL VSESOYUZNOGO KHIMICHESKOGO OBSHCHESTVA IM. D. I. MENDELEYEVA
in Russian Vol 27, No 6, Nov-Dec 82 pp 603-613

KALECHITS, I. V., supervisor of the Laboratory of the Kinetics of High Temperature, USSR Academy of Sciences and DEDOV, A. G., director, Scientific Research Institute of Mechanico-Economic Studies

[Abstract] In the short time of its existence, the Soviet Union has developed an industrial chemical capability of world renown. One of the cornerstones of this development was the early establishment of the State Research Institutes. Output of industrial chemicals, such as ammonia, sulfuric acid, dyes, plastics and hydrocarbon-based products increased dramatically over the sixty years, as shown by 5-year figures from 1928-to 1940 and 10-year figures from 1960 to 1980. This is due both to better methods of production and to increased number of plants. Outputs for each of the individual republics are shown for 1970 and 1975. With the strong price increase of machinery and raw materials, the economics now play a major role in evaluating output. Greater efficiency is recognized as one of the major goals in the 1981-1985 period. References 10 (Russian).
[125-12027]

INSTITUTING BRIGADE FORMS OF ORGANIZATION AND PAYMENT FOR WORK AT KLIN 'KHIMVOLOKNO' PRODUCTION ASSOCIATION

Moscow KHIMICHESKIYE VOLOKNA in Russian No 6, Nov-Dec 82 pp 9-10

TOROPOV, V. A. and TUMANOV, I. M.

[Abstract] Following L. I. Brezhnev's speech at the 26th session of Soviet Trade Unions plants in Klin undertook the title reorganization to cope with labor shortages without a corresponding production decline. Currently the association has 72 complex and 169 specialized brigades, in which 34.3% of all employees are organized. Careful organization and the importance of the brigade leader are stressed. Results at operations, e.g.,

at the acid station and the spinning mill have been freedom from breakdown, 27% increase in production and 12.5% pay increase. Other production parameters have also improved since the reorganization, although there have been problems such as bottlenecks in supplying materials, low quality materials and interruptions of technological production processes. Brigade leaders receive up to 15% supplemental pay, but the authors suggest higher incentives.

[100-12131]

POLYPROPYLENE BINDER TWINE FOR AGRICULTURE

Moscow KHIMICHESKIYE VOLOKNA in Russian No 6, Nov-Dec 82 pp 10-11

KRYMOV, A. V. and POLOVIKHINA, L. A.

[Abstract] The All-Union Scientific Research Institute for Synthetic Fiber Projects together with the Balakovskiy "Khimvolokno" Production Association have developed polypropylene binder twine to replace baling wire and viscous binder twine. The new product allows 40% less twine usage. The technical procedure, which involves twisting fibers made from extrusion aggregates with a slot spinner and subsequent additional twisting, is described in further detail. Field tests indicated savings of 0.77 rubles per ton of straw or 800 rubles per ton of binder twine, without twine breakage.

[100-12131]

MANY-FACETED WORLD OF CHEMISTRY

Moscow KHIMICHESKIYE VOLOKNA in Russian No 6, Nov-Dec 82 pp 11-13

BOLDYREVA, L. G.

[Abstract] The author reports on the international exhibition "Chemistry-82" held in Moscow from 2-16 September, which included 1,700 exhibits from the industrialized world, CMEA countries and, for the first time, Portugal and India. The 900 foreign firms, including 200 German, 150 Japanese, 70 Italian and 68 French exhibitors, are said to "bear witness to the active interest of those countries in trade with the USSR". The author emphasizes the comprehensive program of cooperation among CMEA countries, and the numerous licenses and other forms of foreign trade agreements with capitalist countries. The organizers claim to have applied stringent criteria to the selection of exhibits; the Soviet part of the exhibition dealt with research, chemical and petrochemical technology, equipment and machinery, chemicals for industry, construction and agriculture, ecological chemicals, and chemicals for home and relaxation. Some exhibit topics cited by the author include new brightly-colored fabrics for dresses, wrinkle-resistant fabrics that keep their shape for dresses and suits, a polyamide profile thread that can hardly be distinguished from natural silk, and numerous other

synthetic fibers with nearly unique properties. Absorbent carbon fibers and filtering materials to stop particles less than a micrometer in size were also exhibited.

[100-12131]

UDC 677.4.004.14+677.4.004.14+678.067+677.4.017

SPECIFIC PROPERTIES OF FIBER MATERIALS, BASES FOR THEIR USE FOR TECHNICAL PURPOSES

Moscow KHIMICHESKIYE VOLOKNA in Russian No 6, Nov-Dec 82 pp 13-16

PAPKOV, S. P.

[Abstract] Uses of fiber materials are being expanded to include numerous technical applications based on specific properties. The author discusses such properties as mechanical durability of polymers based on either chemical bonds along the macromolecular chain or the strength of intermolecular reactions, which vary from one specific fiber to another, elastic properties, which are more pronounced in fiber materials than in monolithic materials of similar dimensions, internal fiber structure, discrete structure of fiber material compositions that helps to minimize the importance of minor flaws, high specific surface area of fiber materials that aids sorption, capillary properties and other features of fiber materials. Surface characteristics influence both chemical adsorption and the ability of fiber materials to arrest very small particles of liquid or solid substances through the strength of intermolecular reaction. This feature is useful in such reverse osmosis processes as desalination of water. Capillary action of synthetic fibers allows them to hold large volumes of liquid and to contribute to the comfort of clothing. Fiber materials also have shock resistance and heat insulating properties.

[100-12131]

BASIC DIRECTIONS IN CHEMISTRY RESEARCH IN THE UKRAINIAN SSR ACADEMY OF SCIENCES

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 48, No 12, Dec 82 pp 1235-1238

KUKHAR', V. P.

[Abstract] The author reviews the academy's research in the 60 years since the establishment of the USSR, with reference to important scientists and areas of research such as catalysis, free radical chemistry, electrochemistry, inorganic and analytical chemistry, colloid and organic chemistry. Specific accomplishments are cited for ion melts, stationary and non-stationary

electrode processes, the theory of electrochemical impedance, heterogenic catalysis and catalytic oxidation of ammonia, carbon dioxide and sulfur gas, and thermocatalytic reactors to remove these compounds from waste gases in order to protect the environment. Compounds containing phosphorus and fluorine such as phosphazo-compounds and phosphorus isocyanates and iodides have received special attention. Other areas of research include sorbents and dispersion materials, structures of coordinational materials, macrocyclical complexons, and various pollution-control problems. Bio-compatible polymers and medicinal bonding agents and other polymer research is also an important part of the academy's work. Cooperation with other research institutions in the Soviet Union is summarized.

[104-12131]

UDC 541.64:542.943

MECHANISM OF cis-1,4-POLYISOPRENE DESTRUCTION IN CONDITIONS OF INHIBITED OXIDATION

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 24, No 12, Dec 82 (manuscript received 2 Jun 81) pp 2490-2493

L'VOV, Yu. A., SENDERSKAYA, Ye. Ye. and BALASHEVA, N. F., All-Union Scientific Research Institute for Synthetic Rubber imeni S. V. Lebedev

[Abstract] Seeking to resolve disagreement on causes of the title destruction, the authors sought to demonstrate the hypothesis that the break in the polymer chain during oxidation of the stabilized polyisoprene takes place chiefly at the stage of decomposition of the polymer hydroperoxide involving the oxidation inhibitor that deactivates the radicals that are forming. Their calculations resulted in an equation expressing the connection between the rate of destruction and antioxidant concentration. This equation does not take into consideration the effects of the rate of destruction of inhibitor conversion products or polymer oxidation products. Hence further work involved experimental study of the dependence of initial destruction rate for synthetic isoprene rubber on the concentration of such antioxidants as ionol, bis-(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide and 4,4'-bis(2,6-tert-butylphenol). Results permitted calculation of constants expressing a straight line dependency. Thus the process of decomposition in the presence of inhibitors takes place within the framework of the breakdown of the polymer chain at the hydroperoxide destruction stage, in the presence of an antioxidant, without free radical yields. Figures 2; references 12:

10 Russian, 2 Western.

[112-12131]

COAL GASIFICATION

UDC 662.73/74:002.6

FURTHER IMPROVEMENT OF INFORMATION SUPPLY OF COAL TAR CHEMICAL INDUSTRY IN 11TH FIVE-YEAR PLAN

Moscow KOKS I KHIMIYA in Russian No 12, Dec 82 pp 19-21

SKLYAR, M. G. and SEKIRINA, V. T., Coal Tar Scientific Research Institute

[Abstract] The authors discuss the role of information supply in improving production to furnish the Soviet economy with needed coke and chemical products of coking of sufficient variety and quality. Special attention is to be directed to the development of "selective information distribution" (SID) in order to assist in eliminating production bottlenecks and other difficulties that block the industry's objectives. Areas where better information is required have been identified by questionnaires, interviews, and daily records of specialists. Much of this information has been collected in a "demand-response" card catalog. Information gathered at the institute is reported to the State Public Scientific-Technical Library of the USSR and the Central Ferrous Metal Scientific-Technical Library on an annual basis. Analytical surveys have been made of subjects such as "Coke Quality for Modern Blast Furnaces" and "Analysis of the State and Trends in Coke Production in Foreign Countries With Developed Coal Tar Chemistry." Indices of foreign journals in the fields are translated and made available through inter-library subscriptions. Various types of cooperative arrangements provide further information exchange opportunities, and standardization of information collection and retrieval is being promoted.
[99-12131]

DYNAMICS AND PRODUCTION RESERVES OF NAPHTHALENE AT COAL TAR CHEMICAL ENTERPRISES OF RSFSR AND KAZAKHSTAN

Moscow KOKS I KHIMIYA in Russian No 12, Dec 82 pp 35-38

KOGAN, B. Ye., MOCHALOV, V. V. and AKSENINA, A. A., Eastern Coal Tar Chemistry Scientific Research Institute, Sverdlovsk and SMIRNOV, S. S., Chelyabinsk Metallurgical Plant

[Abstract] The authors studies trends in naphthalene production from 1967 to 1981. While this product is in third place behind pitch and technical carbon, its production is lagging due to marketing problems, antiquated production equipment and technological shortcomings at many plants. The authors discuss production records at several plants, particularly citing a decline in production that began about 1978. Trends in general Soviet coal tar industry production are such that increased naphthalene production is not anticipated from resources. Consequently, higher yields must be accomplished by technological advances, such as new distilling, rectifying and recycling procedures that will permit increases in the extraction coefficient to 75-80% and naphthalene production to 64% of input materials. Figures 2; references 5 (Russian).
[99-12131]

COMBUSTION

UDC 541.126+536.48

IGNITION OF CONDENSED SUBSTANCES HAVING VARIOUS GEOMETRIC CONFIGURATIONS BY THERMAL CONVECTION CURRENTS

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 56, No 12, Dec 82
(manuscript received 2 Nov 81) pp 2959-2964

LYUBCHENKO, I. S., LYUBCHENKO, V. I., MATVEYEV, V. V. and MARCHENKO, G. N.

[Abstract] Consideration is given to the mathematical description of ignition of condensed substances varying in geometric configuration (flat, cylindrical, spherical), assuming a first order exothermic reaction. The asymptomatic expansions can be used in calculation of the lag time, ignition temperature, thermal convection impulse required for ignition, and the depth of combustion; a linearized formula is derived for the calculation of kinetic constants from experimental data. References 9 (Russian).
[129-12172]

UDC 541.124:541.126:546.211

MECHANISM OF METHANE COMBUSTION; PART 7: COOL FLAME OXIDATION

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian
No 12, Dec 82 (manuscript received 10 Nov 81) pp 2658-2663

BASEVICH, V. Ya. and KOGARKO, S. M., Institute of Chemical Physics,
USSR Academy of Sciences, Moscow

[Abstract] Reactions involved in the combustion of methane by oxygen and HNO_3 were analyzed to determine the mechanism of cool flame oxidation under a variety of conditions. The final interpretation of the rate constants and thermophysical parameters which were derived was in agreement with a mechanism involving initial acceleration of oxidation, followed by inhibition of the process due to thermal decomposition of the peroxide radical because of formaldehyde formation and its rapid reaction with active centers, which in turn leads to a decrease in the concentration of the latter. Figures 5; references 18: 8 Russian, 10 Western.
[128-12172]

FERTILIZERS

ADVANCES IN MINERAL FERTILIZER INDUSTRY AND CHEMICALS FOR AGRICULTURE IN SIXTY YEARS OF SOVIET POWER

Moscow KHIMIYA V SEL'SKOM KHOZYAYSTVE in Russian No 1, Jan 83 pp 3-5

[Article by A. G. Petrishchev, minister for production of mineral fertilizers:
"Implementation of Decisions of 26th CPSU Congress--60 Glorious Years"]

[Text] The Soviet people have solemnly celebrated a glorious date, the 60th anniversary of the formation of the USSR. This is a remarkable event, vivid testimony of the triumph of the historical deeds of socialism, Lenin's national policy of the CPSU.

A new third year of the five-year plan has commenced. In accordance with the decision of the May (1982) Plenum of the CPSU Central Committee, which approved the USSR Food Program, our industry is faced with tasks for continued speedy and comprehensive use of chemistry in agriculture. The party considers it necessary to increase substantially, as speedily as possible, delivery to rural areas of mineral fertilizers and chemicals for protection of plants, since there is no question of the close link between improving the effectiveness of agricultural production with increase in standards of mineral fertilizers and use of pesticides.

Thanks to the intensive use of fertilizers and other agrotechnical measures, our country is in first place in the world with regard to cotton harvest; we recover large harvests of flax, sugar beets, tea and citrus fruit. Numerous experiments have shown that, under conditions prevailing in the USSR, 1 q [quintal] of ammonium nitrate yields an increment of up to 5 q grain/ha [hectare], 25-30 q sugar beets, 18-20 q potatoes, whereas 1 q granulated superphosphate applied to beds during sowing yields up to 5 q grain [additionally?]. According to estimates made by specialists, about one-third of the gross agricultural harvest in our country, under the years of the 10th Five-Year Plan, was obtained thanks to use of fertilizers, chemical agents for protection of plants and land improvement agents.

Use of new herbicides with broad spectrum of action on weeds makes it possible to introduce complex mechanization in cultivating the most labor-consuming crops. Chemical weeding of soybean, sugar beet, sunflower, rice and other crop plantings increases by 1.5 times the productivity of labor and preserves the harvest. According to estimates of economists, every ruble spent on chemical treatment of agricultural crops saves production worth 7-8 rubles.

The mineral fertilizer industry has been given some large and responsible tasks under the 11th Five-Year Plan. In 1985, 26.5 million tons of mineral fertilizers, 950,000 tons mineral feed supplements and 680,000 tons chemicals for plant protection will have to be delivered to agriculture.

Special attention is being given to further improvement of the quality of mineral fertilizers, production of highly concentrated and compound fertilizers. In addition, the necessary steps will have to be taken to produce fertilizer only in granulated and large-crystal form starting in 1988. There are plans to expand production of compound liquid fertilizers and long-action fertilizers.

The increase in production of chemical agents for plant protection must be effected by means of producing modern and highly effective agents, which would permit meeting the demands of agriculture to a significant extent with respect to herbicides needed to adopt industrial technologies for raising agricultural crops. There are plans to augment the production of mineral fertilizers and chemical agents for plant protection in small packages to meet the demands of private subsidiary farms.

Before the Great October Socialist Revolution, the chemical industry of Russia, in particular, mineral fertilizer production, was very poorly developed. For example, in 1913, only about 4000 tons nitrogen fertilizers and about 13,000 tons phosphorus fertilizers and only 145,000 tons sulfuric acid were produced. The small, semi-cottage-industry enterprises worked mainly with raw material brought in from other locations. No potassium fertilizers were produced at all.

After the victory of the Great October Revolution, the chemical industry began to develop at an intensive pace in our country. In the period prior to the Great Patriotic War, large chemical plants and combines equipped with modern technology had been constructed for production of potassium and nitrogen fertilizers. In 1932, the "Apatite" Mining and Chemical Combine, which was established on the basis of the Khibinskiy mine, started to produce. This made it possible not only to abandon the import of phosphorous raw material, but to subsequently start exporting it to many countries of the world. The Solikamsk Potassium Combine was constructed at the site of the Verkhne-Kamsk mine, which is the country's largest potassium salt mine.

After the end of the Patriotic War, the mineral fertilizer industry started to develop very intensively. At that time, there was development of a new sector: production of organic toxic chemicals. There was better technical outfitting of most enterprises and sophistication of production, as well as better labor productivity and costs diminished.

The period after 1959, when intensive development of this industrial sector, particularly mineral fertilizer production, started in accordance with the well-known decisions of the party and government holds a special place in the history of the chemical industry of the Soviet Union. Discovery of new deposits made it possible to strengthen appreciably the raw material base, and research work began to be conducted extensively at scientific research institutes concerned with this sector. In 1959-1965, 2.3 times more funds was invested for construction of chemical industry enterprises than in the entire preceding period. This made it possible to increase production of mineral fertilizers by 2.5 times and that of chemical agents for plant protection by 4.5 times.

Under the 8th and 9th Five-Year Plans, there was continued expansion of construction of new enterprises in this sector, as well as scientific research, development of new products and entire sectors, improved effectiveness of social production on the basis of comprehensive acceleration of technological progress and wise organization of labor. There was intensive development of production of concentrated and compound fertilizers, herbicides, new types of organic agents for plant protection, mineral supplements for livestock feed. New deposits of mineral and chemical raw materials began to be mined, and on their basis large enterprises were constructed for production of potassium salts in Belorussia, phosphorites in Kazakhstan and sulfur in the Ukraine. Natural gas started to be used extensively.

The RSFSR is in the lead in production of mineral fertilizers and chemical agents for the protection of plants, and most of the very large enterprises in this sector of industry are located there. However, at present there are some substantial changes in the geographic location of enterprises of the mineral fertilizer industry. They are developing at an overtaking rate in Belorussia, the Ukraine, Kazakhstan, in republics of Central Asia, Transcaucasian and Baltic regions.

The mineral fertilizer industry in Kazakhstan and Central Asian republics, which is based on large deposits of mineral, chemical and hydrocarbon raw material, cheap fuel and electricity, occupies one of the leading places in our country for recovery and processing of phosphorites and production of a wide assortment of basic chemical products.

Our industry has a strong raw material and fuel-energy base: unique apatite mine on Kola Peninsula, large stock of phosphorites in Southern Kazakhstan and Leningrad Oblast, phosphate raw material in Siberia and the Far East, unequaled stock of potassium salts in the Urals, Belorussia and the Ukraine. There are resources referable to iron pyrites, natural sulfur, gases of metallurgical production and other sectors of industry in the Urals, Kazakhstan, Western Ukraine, Central Asia and the Volga region. Thanks to the existence in our country of a broadly branched network of gas lines, the mineral fertilizer plants are provided with natural gas.

After the March (1965) Plenum of the CPSU Central Committee, which laid the foundation for today's agrarian policy, enormous work was done in our country to strengthen the material and technical base of the agroindustrial complex, industrialization and use of chemistry in agriculture, creation of new sectors that service it. In the past period, deliveries of mineral fertilizers to rural areas have increased by 3 times and for chemical feed supplements by over 15 times.

The comprehensive support and attention of the CPSU Central Committee and Soviet government has made it possible for this sector of industry to double its capacity for fertilizer production within a relatively short time. Already in 1973, the Soviet Union advanced to first place in the world in production of fertilizers.

Under the 10th Five-Year Plan, a large program of capital construction was fulfilled. Twelve large enterprises were put in operation, including the world's largest producer of nitrogen fertilizers, the Tol'yattiazot Industrial

Association, Odessa Port Plant, Don River Chemical Plant and several others, as well as the unique Tolyatti-Gorlovka-Odessa ammonia pipelines extending over almost 2500 km, along which 30 distribution stations have already been installed each of which can unload 10,000 tons ammonia per year. More than 400 large plants have been put in operation. The capacity for mineral fertilizer production increased by more than 37 million tons of standard fertilizers and by 66,500 tons (in arbitrary units) of chemical agents for plant protection.

Virtually the entire increment in mineral fertilizers was obtained as a result of increasing production of compound and concentrated forms of fertilizers. This made it possible to raise the level of nutrients in fertilizers up to 39% in 1982. There has also been an increase in share of the most important types of products manufactured with equipment that has large unit capacity.

Important new tasks have been put to this sector under the 11th Five-Year Plan. We shall have to put in operation facilities to produce 9 million tons of fertilizer, 8 million tons of ammonia, 7 million tons of sulfuric acid and 2 million tons of sulfur. In all, under the 11th Five-Year Plan, 165 new industrial complexes will have be delivered. Considerable capital investments are being allocated for sociocultural construction and development of projects for environmental protection.

The main task at the present stage is to implement these large plans for capital construction. The staff of many building organizations are doing everything in their power for accelerated completion of installations for the fertilizer industry. The staff of the Krasnodarkhimstroy [Krasnodar Chemical Trust] has assumed the obligation to put in operation 1 year before the target date of installations for the production of compound granulated fertilizers at the Krasnodar Chemical Plant. The construction workers of Novgorod, Novomoskovsk, Meleuz, Cherepovets, Kirovsk and Uzbekistan have assumed large socialist obligations to expedite completion of installations for the production of mineral fertilizers and raw material. At the same time, it must be noted that construction of a number of enterprises for the production of mineral fertilizers is unsatisfactory. Those groups of workers must correct the existing lags.

The staffs of the following industrial associations have reported completion of 1982 assignments prior to the target dates: Korund in Chernorechensk, Minudobreniya in Voskresensk, the ones in Grodno, Shchekino, Azot in Severodonetsk, Khimprom in Sumy, Gruzgornokhimprom, Pervomayskiy, Kedayskiy, Almalyk, Vurnary, Dzhambul (superphosphate) chemical plants and many other enterprises. The tasks advanced by the State Plan for 1983 are in the center of attention of workers in this sector. The worker groups in our enterprises are doing everything in their power to meet the rural area needs in chemicals.

The party guides us toward a constant search for internal reserves to increase production. This sector does have such reserves and, it must be stated, they are not small. There are great possibilities for augmenting fertilizer production by economizing on material resources. Under conditions of many-ton production, if the cost standard is reduced by only 1% it would be possible to save annually 125,000 tons of sulfuric acid, 130,000 tons of ammonia and almost 300 million cubic meters of natural gas. This means that it would be possible to deliver tens of thousands of tons of mineral fertilizers and feed

supplements for fields and farms. The knowhow gained by the Severodonetsk and Novomoskovsk "Azot" [nitrogen] industrial associations on maximum utilization of secondary energy resources and other valuable innovations [or initiative] of the groups of workers and leading workers referable to saving and thrift have undergone broad dissemination in other enterprises of this sector.

A substantial flaw in organizing use of fertilizers is the significant loss during storage, transportation and application in soil. According to the estimates of specialists, at the present time the loss of fertilizer between the plant and field constitutes up to 14% in some regions. It is the immediate duty of workers at enterprises and organizations of Soyuzsel'khozkhimiya [All-Union Association for Agricultural Chemistry?], transportation workers and workers in the fields and farms to create a reliable barrier against losses.

Fulfillment of the tasks put to the mineral fertilizer industry will make it possible to solve major problems related to rapid advancement of agricultural production, and this would result in further improvement of the welfare of all peoples in our multinational homeland. On behalf of the board of the ministry, I congratulate the workers in all sectors involved in furnishing chemical products to agriculture on the occasion of the new year, 1983; I wish them good health, major achievements in their work and personal happiness.

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10,657

CSO: 1841/138

UDC 66.011

CAPACITY SELECTION OF TECHNOLOGICAL LINES AND THEIR BACKUP IN FERTILIZER INDUSTRY

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 1, Jan 83 pp 5-7

GRISHAYEV, I. G.

[Abstract] An analysis of technological productivity is reported with the idea of maximizing the output of equipment and operations. With large scale equipment, production costs are lowered with increased performance reliability, which can be achieved through development of new technology and methodology. Maintaining a backup for entire production line or for some of the segments which have frequent breakdowns is another way of assuring continuous productivity during planned or accidental repairs, maintenance or quality control operations. For such cases it is necessary to reserve some of the intermediate products which could supply the operations down the line from the trouble spot. Such "reserve depots" should be selected on the basis of performance history. For each level of performance-reliability of a technological line, optimal operation parameters can be identified and the desirability of reserve maintenance can be estimated. Figures 3; references 4 (Russian).

[153-7813]

UDC 631.859.13:661.634.2

REASONS FOR RETROGRESSION OF ASSIMILABLE FORM OF PHOSPHATE COMPONENT IN AMMOPHOS PRODUCED FROM SEMIHYDRATE EXTRACTION PHOSPHORIC ACID

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 1, Jan 83 pp 8-11

PERMINOVA, L. Ya., ZHDANOV, Yu. Zh. and POPOVA, G. Ya.

[Abstract] The quality of ammophos depends on its content of P_2O_5 and nitrogen. During its production, however, a retrogression of assimilable P_2O_5 takes place reaching about a 3% level (lowering of P_2O_5 ass content in relationship to P_2O_5 total). To explain this occurrence, the production

conditions for extraction phosphoric acid (EPA) and the drying method of the ammophos pulp were studied in relationship to the quality of product. It was established that ammophos obtained from dihydrate and semihydrate EPA differs in the content of SO_3 , CaO and P_2O_5 total. Furthermore, CaO forms phosphorus containing compounds, lowering the level of P_2O_5 ass in ammophos. The effect of drying temperature and neutralization was almost insignificant. Figures 2; references 13: 12 Russian, 1 Western.
[153-7813]

UDC 66.099.2

PRODUCTION OF GRANULATED PHOSPHORIC-POTASH FERTILIZERS BASED ON THERMOPHOSPHATES

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 1, Jan 83 pp 14-16

KLASSEN, P. V., VASIL'YEVA, L. V., SHOMIN, I. P., GRISHUNINA, L. Ye., PIROGOV, V. I. and GALINA, V. N.

[Abstract] Thermophosphates are obtained presently in form of finely dispersed, dry powders. To improve their transport, storage and application parameters, they must be converted to granular form. In the present paper optimal conditions are reported for granulation of thermophosphates. Following factors showed positive effect on the formation of granules: increased temperature, a 30% content of KCl and 11-13% humidity level in the shaft. The product obtained in this fashion was nonhygroscopic and did not compress on storage. Figures 5; references 8: 4 Russian, 4 Western.
[153-7813]

UDC 661.634.2:661.635.68

PRODUCTION SPECIFICATIONS FOR SUPERPHOSPHORIC ACID CONTAINING 63-65% P_2O_5

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 1, Jan 83 pp 11-23

KOCHETKOV, S. P., LEMBRIKOV, V. M., KORSHUNOV, L. I., LYKOV, M. V. and ZORIKHINA, Z. A.

[Abstract] It was established that superphosphoric acid (SPA) must show a minimum of 63-65% P_2O_5 content in order to yield transparent complex liquid fertilizers. In this paper, temperature conditions necessary for the production of SPA with this level of P_2O_5 are reported. It is shown that the production temperature should be in the range of 175-185°C; the acid should be preheated and possibly recirculated through the reactor, because contact time appears to be a crucial factor. Addition of small quantities of ammoniacal compounds are also recommended. Figure 1; references 6: 5 Russian, 1 Western.
[153-7813]

SELECTION OF STRUCTURAL MATERIAL IN PRODUCTION OF AMMONIUM NITRATE BY SINGLE STAGE NON-STEAMING METHOD AND PRODUCTION SAFETY PROBLEMS

Moscow KHIMICHESKAYA PROMYSHLENNOST' in Russian No 1, Jan 83 pp 28-32

KIL'MAN, Ya. I. and ZAICHKO, N. D.

[Abstract] One of the serious problems connected with the single stage process of production of ammonium nitrate is the corrosion of equipment. Experimental data are reported on the behavior of various materials under reaction conditions predominant in this process. Addition of ammonium nitrate to HNO_3 at boiling point showed little corrosive effect on steel in the first 100 hours of operation; it intensified considerably during longer runs (200 hours and more). Niobium appeared to be a much better non-corrosive material for this process. It was discovered that corrosive processes took place principally in the upper stage of the reactor-neutralizer, probably due to local overheating of HNO_3 . The second important issue concerned safety. It was concluded that a safe operation could be maintained by keeping the reaction product the shortest possible time in reactor-neutralizer, keeping the process in alkaline medium and lowering the temperature to 170°C by the use of reduced pressure. References 16: 13 Russian, 3 Western.

[153-7813]

SELECTING EQUIPMENT IN INVESTIGATING MECHANICAL ACTIVATION OF PHOSPHATE RAW MATERIALS

Novosibirsk IZVESTIYA SIBIRSKOGO OTDELENIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKIKH NAUK in Russian No 6, Nov 82 pp 71-74

KOZLOV, V. I. and KOZYREV, S. A., Krasnoyarsk Polytechnical Institute

[Abstract] Obstacles to mechanical activation of phosphates to produce fertilizers include the lack of continuous-operation production equipment. The authors discuss comparative features of differential centrifugal mills and centrifugal mills with hemispherical characteristics, using phosphorites from the Krasnoyarsk area and varying the design of the centrifuge drum. Horizontal drums were clearly superior, and somewhat more soluble P_2O_5 was produced using grinders of tungsten-cobalt alloys. Yet increased density of grinding ball materials brought with it increased use of energy. The centrifugal mill with fixed grinding balls, separator feed in the same chamber as the grinders and openings in the side of the same size as the grinding balls was found to be more effective and more durable. Further study is proposed of the reactivity of phosphorites of various mineralogical types. Figures 2; references 6 (Russian).

[113-12131]

FREE RADICALS

UDC 514.14

CERTAIN PRINCIPLES OF PHOTOCHEMICAL REACTIONS OF FREE RADICALS IN SOLID PHASE

Moscow ZHURNAL FIZICHESKOY KHIMII in Russian Vol 56, No 12, Dec 82
(manuscript received 11 Jan 82) pp 2915-2927

MEL'NIKOV, M. Ya., Chemical Faculty, Moscow State University
imeni M. V. Lomonosov

[Abstract] When exposed to various factors many substances in solid phase form free radicals which may attain high concentrations as a result of the solid phase environment. The importance of photochemical reactions of free radicals are due to the fact that the electronic spectrum of such radicals is shifted to a longer wavelength in comparison with the parent compound, and the fact that such radicals also possess much higher extinction coefficients. In addition, photochemical transformations of free radicals are accompanied by quantum yields that often exceed that seen in photolysis of the parent compound. Finally, on exposure to light the free radicals may give rise to even more active particles, which are unstable under photolytic conditions and may regenerate the original radicals as a result of interaction with surrounding molecules. To date, the following types of free radical photochemical reactions have been substantiated experimentally: substitution, dissociation, ionization, and isomerization. References 67: 40 Russian, 27 Western.
[129-12172]

DIASTEREOMERIC SPLITTING OF EPR SPECTRA OF PHOSPHORANYL RADICALS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 12, Dec 82 (manuscript received 6 Apr 82) pp 2692-2696

TUMANSKIY, B. L., KRON, T. Ye., SOLODOVNIKOV, S. P., BUBNOV, N. N. and KABACHNIK, M. I., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] Diastereomeric splitting was seen on EPR spectra of phosphoranyl radicals with two asymmetric centers as a result of small differences in the hyperfine interaction constant. The extinction kinetics of 1,3,2-oxaphospholanes followed first order kinetics in the -40° to -100°C range; the presence of a signal due to tert-butyl radical on the EPR spectrum indicated that extinction involved β -removal of the tert-butyl substituent on the O atom. Figures 2; references 6: 4 Russian, 2 Western.
[128-12172]

NITROGEN COMPOUNDS

UDC 547.8+547.245

ORGANIC SILICON SYNTHESIS OF 1-ADAMANTYLISOCYANATE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 11 Jan 82) pp 2653-2654

MIRONOVA, N. V. and MIRONOV, V. F.

[Abstract] Previous research showed that synthesis of isocyanates from amines and phosgene was facilitated by using N-silyl derivatives of the latter (this journal, 1969 p 2598; DOKLADY AKADEMII NAUK SSSR 1968 p 115, 1970 p 110; ORGANOMETAL. CHEM SYN., 1972 p 329; ORGANOMETAL. CHEM. REV., 1979 p 373). Silyl protection of the amines also enabled isocyanate production without use of phosgene (this journal, 1973 p 2089, 1975 p 2007, 1980 p 955, p 2022). The present study describes production of the title compound by these methods in place of use of scarce adamantocarboxylic acid amide. Chemical procedures and NMR spectral data are given. References 8: 5 Russian, 3 Western.
[105-12131]

UDC 542.943.7:547.233.1

OXIDATION OF PRIMARY AMINES BY POTASSIUM FERRICYANIDE

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian
No 12, Dec 82 (manuscript received 12 Apr 82) pp 2758-2762

NIKITIN, G. I., TROYANSKIY, E. I. and IOFFE, V. A., Institute of Organic Chemistry imeni N. D. Zelinskiy, USSR Academy of Sciences, Moscow

[Abstract] Studies were conducted on the oxidation of primary n-alkyl-, sec-alkyl, and tert-alkylamines under mild conditions using $K_3Fe(CN)_6 \cdot 3H_2O$ in NaOH at 70-80°C. Oxidation of the n-alkylamines resulted in the formation

of the corresponding nitriles; in addition, oxidation of n-heptylamine also yielded small quantities of n-heptylurea. Oxidation of the sec-alkylamines resulted in the synthesis of hydrazones as a result of oxidative dimerization. Tert-butylamine was found to be inert in the oxidative system employed.

References 15: 5 Russian, 9 Western.

[128-12172]

UDC 547.258.11+541.632

REACTIVITY OF ORGANIC TIN COMPOUNDS, PART 24: SYNTHESIS OF (+)-4-TRIMETHYLSTANNYLPYNE

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 18, No 11, Nov 82
(manuscript received 9 Mar 82) pp 223-2237

KASHIN, A. N., BAKUNIN, V. N., BELETSKAYA, I. P. and REUTOV, O. A.

[Abstract] Previously the authors produced optically active indenyl derivatives of tin and studied their reactions with various electrophile agents (this journal, 1979, pp 15, 16, IZVESTIYA AKADEMII NAUK SSSR SERIYA KHIMICHESKAYA, 1977 p 2638). Continuing that research they have synthesized the title compound (I) through the reaction of (+)-trans-4-chloropyrene (II) with $(\text{CH}_3)_3\text{SnLi}$, and studied ^{13}C NMR spectra of the title compound. The spectra showed that the product consisted at least 90% of a single isomer. The organic tin derivative of alpha-pyrene was synthesized through the reaction of nucleophile substitution of chlorine in compound (II) with the action of $(\text{CH}_3)_3\text{SnLi}$ cuprate in 1,2-dimethoxyethane. The isomer composition of resulting compounds as determined by ^{13}C NMR and gas liquid chromatography showed a trans : cis ratio of 65 : 35, with little variation when $(\text{CH}_3)_3\text{Sn}$ was used, and of 75 : 25 when the cuprate was used. Cis-trans-isomerization took place with considerable speed in the presence of AlCl_3 in a 10% molecular solution in benzene; this resulted in the synthesis of trans-4-trimethylstannylpyrene, with an intermediate organic aluminum compound forming that isomerized into a more durable trans-isomer. Procedures are given in the experimental section. References 18: 4 Russian, 14 Western.
[109-12131]

REACTIVITY OF ORGANIC TIN COMPOUNDS, PART 25: STEREOCHEMISTRY OF
PROTODEMATALIZATION OF (+)-4-TRIMETHYLSTANNYLPYNE

Leningrad ZHURNAL ORGANICHESKOY KHIMII in Russian Vol 18, No 11, Nov 82
(manuscript received 9 Mar 82) pp 2237-2241

KASHIN, A. N., BAKUNIN, V. N., BELETSKAYA, I. P. and REUTOV, O. A.

[Abstract] Continuing previous research that showed that indenyl derivatives of tin reacted with various electrophile agents by an allyl regrouping, the authors synthesized the title compound (I) and studied its reactions with HCl and CF_3COOH in benzene, dioxane and acetonitrile. Stereochemistry was studied for mixtures of cis- and trans-isomers at a ratio of cis : trans = 35 : 65, and for a pure trans-isomer by gas liquid chromatography using an internal standard. The reaction with hydrogen chloride decreased in the order of solvents with $\text{CH}_3\text{CN} > \text{C}_6\text{H}_6 > \text{C}_4\text{H}_8\text{O}_2$. Analysis of the data indicate that whereas in the reactions of the cis-isomer of (I) an anti-substitution takes place, with the trans-isomer a syn-substitution predominates. Various effects were observed for the methyl group on the beta-carbon atoms. Neither beta-pyrene nor trans-delta-pyrene were found among reaction products, indicating that reduction of trans-4-bromopyrene takes place as a syn-substitution of bromine by the hydride ion. Procedures are summarized in the experimental section. References 14: 4 Russian (one English translation), 10 Western.
[109-12131]

UDC 541.49:(661.9.321+546.185.286.5)

REACTION OF PHOSPHORUS HYDROXYTRIISOTHIOCYANATE WITH CHLORIDES AND
HYDROXYCHLORIDES OF MOLYBDENUM AND TUNGSTEN

Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 48, No 12, Dec 82
(manuscript received 15 Jan 82) pp 1239-1241

SKOPENKO, V. V., BRUSILOVETS, A. I., SINKEVICH, A. V. and TRACHEVSKIY, V. V.,
Kiev State University imeni T. G. Shevchenko

[Abstract] The title compound forms durable compounds with tetrachlorides of titanium, zirconium, hafnium and tin. The authors studied the title reaction in carbon tetrachloride and measured its results with electron spin resonance. The reactions with molybdenum and tungsten variants followed different courses. The former led to formation of $\text{MoOCl}_3 \cdot 2\text{OP}(\text{NCS})_3$, while the latter, in forming $\text{WCl}_5 \cdot \text{OP}(\text{NCS})_3$, resulted in a compound that gave no ESR signal. Cryoscopic examination indicated that partial dissociation took place with separation of $\text{OP}(\text{NCS})_3$ molecules in the tungsten variant. All adducts obtained were crystalline substances that were durable in the

absence of moisture, and which hydrolyzed readily in the atmosphere and dissolved in numerous solvents. Further clarification of the coordination capacity of the products came from infrared spectra. References 11: 7 Russian, 4 Western.
[104-12131]

UDC 541.6+547.879

SPATIAL STRUCTURE OF PHOSPHORUS-CONTAINING HETEROCYCLES, PART 30:
INTRAMOLECULAR ELECTRONIC REACTIONS IN 2-PHENYL-1,3,2-DIOXAPHOSPHORINANES
ACCORDING TO ELECTRONIC SPECTROSCOPY DATA

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 15 Mar 82) pp 2428-2433

ARBUZOV, B. A., ARSHINOVA, R. P. and VINOGRADOVA, V. S., Scientific
Research Chemical Institute imeni A. M. Butlerov, Kazan State University
imeni V. I. Ul'yanov-Lenin

[Abstract] Previous study of the title compounds with tri- and quadrivalent phosphorus provided information for further study of precise effects of conjugation between the phosphorus atom and neighboring pi-electron groupings, (IZVESTIYA AN SSSR SERIYA KHIMICHESKAYA, 1979, p 1518, this journal, Vol 49, 1979 p 2661). In line with that research, the authors investigated ultraviolet spectra of these compounds to test the hypothesis that, in compounds wherein phenyl reacted via a mesomer mechanism with a neighboring unsaturated grouping, there occurred intensification and bathochromic shift in the K- and E-bands of benzene absorption. Appearance of an intense R-band (a p- pi* -shift) in the ultraviolet spectrum of 2-phenyl-5,5-dimethyl-1,3,2-dioxaphosphorinane indicated a forced coplanar orientation of pi-orbitals of the benzene ring and an orbital of an unseparated electron pair of trivalent phosphorus, where no direct correlation was found between the intensity of the R-band and mutual orientation of p- and pi-orbitals. The ultraviolet spectrum of 2-phenyl-2-hydroxo-1,3,2-dioxaphosphorinane showed little such conjugation, while 2-phenyl-2-thiono-1,3,2-dioxaphosphorinane showed superposition of the K-band of benzene absorption, which thus could not be regarded as a sign of conjugation. Figure 1; references 17: 15 Russian, 2 Western.
[105-12131]

REACTION OF DIALKYL-N-BUTYL-N-ISOBUTENYLAMIDOPHOSPHITES WITH ACIDS AND PHENOLS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 20 Nov 81) pp 2433-2438

GRYAZNOV, P. I., KIBARDIN, A. M., GAZIZOV, T. Kh. and PUDOVNIK, A. N.,
Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan
Branch, USSR Academy of Sciences

[Abstract] Dialkylamidophosphites react with carboxylic acids forming dialkylacylphosphites and amines with excess acid bringing a shift in the direction of acylphosphites, and an excess of amines bringing more amidophosphite formation. The authors studied these reactions using ^{31}P NMR to assess reactions of alkylvinylamides of dialkylphosphorous acids with carboxylic acids and phenols. Data indicate that these amides react more rapidly with stronger acids, with changes of ester radicals of diesteramidophosphites in the order of C_2H_5 , C_3H_7 , and $\text{iso-C}_3\text{H}_7$ causing retardation of the reaction, apparently due to spatial factors. Other spectral data showed, for example, that phenols with electron-acceptor substituents in the para-position react with dialkylvinylamidophosphites more rapidly than standard phenol and *p*-cresol. Reactions of dialkyl-N-butyl-N-isobutenylamidophosphites with carboxylic acids increased in rate as acidity was increased and with changes in the phosphorus ester radical in the order of $\text{iso-C}_3\text{H}_7 < \text{C}_3\text{H}_7 < \text{C}_2\text{H}_5$. No intermediate products were observed. Corresponding dialkylarylphosphites formed, and the reaction rate increased with changes in the para-substituent of phenol in the order $\text{CH}_3 \leq \text{H} < \text{Cl} < \text{NO}_2$, and in the presence of acidic additives. In small (2%) quantities triethylamine retarded the reactions, while in significant amounts (10%) it speeded the reaction. Figures 4; references 14: 12 Russian, 2 Western.
[105-12131]

REACTIONS OF THIOESTERS OF ACIDS OF TRIVALENT PHOSPHORUS WITH α,β -UNSATURATED CARBOXYLIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 8 Jan 82) pp 2438-2444

SINYASHIN, I. G., SINYASHINA, T. N., BATYYEVA, E. S., PUDOVNIK, A. N. and OFITSEROV, Ye. N., Institute of Organic and Physical Chemistry
imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] Little study has been made of the title reactions. The authors studied the mechanism of the reaction of the ethyl ester of diethylthiophosphonous acid with acrylic and methacrylic acids using ^{31}P NMR and infrared

spectroscopy, as well as differential thermal analysis. Results and the absence of doublet signal splitting suggested the structure of a mononuclear phosphorane, which was confirmed when the course of the reaction was controlled with methacrylic acid. Thermographic study showed that the reaction of thiophosphonite with acrylic acid began at a lower temperature than the reaction with methacrylic acid. The reactions were found to have at least 3 stages, with the first two following different courses. Experimental data was insufficient to determine which of 2 alternative mechanisms was involved in the disintegration of monocyclic phosphorane after its formation. The general conclusion was that the title reaction depends for its direction on the number of thioalkyl groups on the trivalent phosphorus atom. Thioesters of phosphonous acids reacting with acrylic and methacrylic acids lead to products of addition, while thioesters of phosphonous and phosphorous acids cause polymerization of the initial α,β -unsaturated carboxylic acids. Chemical and spectral procedures are summarized in the experimental section. Figures 2; references 21: 12 Russian, 9 Western.
[105-12131]

UDC 547.241

1,3-DIPOLAR CYCLOADDITION OF DIAZOALKANES TO ISOPROPENYLPHOSPHONATES AND CERTAIN PHYSICOCHEMICAL PROPERTIES OF ORGANOPHOSPHORUS COMPOUNDS OF THE CYCLOPROPANE SERIES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 26 Jan 82) pp 2444-2458

GAREYEV, R. D., CHERNOVA, A. V., ISHMAYEVA, E. A., BERDNIKOV, Ye. A., SHAGIDULLIN, R. R., STRELKOVA, Ye. N., DOROZHKOVA, G. M., PATSANOVSKIY, I. I. and PUDOVIK, A. N., Kazan State University imeni V. I. Ul'yanov-Lenin; Kazan Veterinary Institute imeni N. E. Bauman; Institute of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] The authors had learned previously that in related reactions the stereochemical direction was determined primarily by the nature of substituents at the chiral phosphorus atom which shielded double bonds from both sides. This factor was also related to the position of the reaction center. To further define the nature of these reactions the authors studied 1,3-dipolar cycloaddition of O,O-dimethyl- α -diazoethylphosphonate to O,O-dimethyl-isopropenylphosphonate, with a slight excess of the dipolarophile, at 50-55°C. Data of element analysis, infrared, NMR ^1H , ^{31}P NMR and PMR spectra were used to control and observe features of the reactions. Results showed strictly stereospecific reaction for such compounds as trans-3,5-dimethyl-3,5-dimethoxyphosphinyl- Δ -pyrazoline in photolysis as it converted into trans-1,2-dimethyl-1,1-dimethoxyphosphinylcyclopropane. Further information on the yields of phosphorus-containing derivatives of cyclopropane in relation to α,β -unsaturated compounds were obtained by studying 3-methyl-3-dimethoxyphosphinyl- Δ -pyrazoline. Changes occurring during photolysis were

attributed to the number and nature of substituents at C³ and C⁵ atoms of the heterocycle. Procedures and spectra are summarized in the experimental section. Figures 4; references 35: 23 Russian, 12 Western.
[105-12131]

UDC 547.241.07 (088.8)

HYDROPHOSPHORYLATION OF ALLENE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 25 Jan 82) pp 2459-2464

NIFANT'YEV, E. Ye., MAGDEYEVA, R. K., MASLENNIKOVA, V. I., TABER, A. M.
and KALECHITS, I. V., Moscow State Pedagogical Institute imeni V. I. Lenin

[Abstract] Homolytic hydrophosphorylation of alkadienes including allene offer a means of synthesizing unsaturated organic phosphorus compounds for various uses. The authors studied this reaction with dialkylphosphites, phosphonous acids, hypophosphorous acids and salts in the presence of peroxide initiators. Results were evaluated in part by ³¹P NMR and PMR spectroscopy. The hypothesis that allyl and isopropenyl adducts formed as a result of addition of the phosphorus-containing fragment to the end and middle carbon atom, respectively, of the allene molecule, was confirmed. More accumulation of phosphinic acid salts occurred when methanol was the solvent than when isopropyl alcohol was used. The final stage of the test was to compare reaction rates of various hydrophosphoryl compounds with allene. Allylalkylphosphinic acids were isolated and described for the first time. Chemical and spectral results are given in the experimental section. Figures 1; references: 5 Russian, 11 Western.
[105-12131]

UDC 547.466+547.76.88

N-HYDROPHOSPHORYL DERIVATIVES OF N-ALKYLAMINOACETIC ACID IN SYNTHESIS OF 1,4,2-DIAZAPHOSPHORINANE-5-ONES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 19 Apr 82) pp 2465-2467

GLOLOBOV, Yu. G. and NESTEROVA, L. I., Institute of Organic Chemistry,
UKSSR Academy of Sciences, Kiev

[Abstract] Previously unknown acidic phosphites with an amino acid fragment have prospects for synthesizing numerous new N-phosphorylated N-alkylglycinates. The authors discuss infrared, PMR and ³¹P NMR spectra of compounds obtained by the reaction of alcohol and water with dichloroaminophosphites. The resulting compounds had not previously been described. The title compound was

synthesized from N-hydrophosphoryl derivatives of N-alkylglycinates and benzalmethylamine. Chemical and spectral data are given in the experimental section. References 7 (Russian).
[105-12131]

UDC 547.26'118

CERTAIN PATTERNS OF EFFECT OF SUBSTITUENTS ON REACTIVITY OF PHOSPHORUS COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 9 Jan 78) pp 2469-2471

GUBAYDULLIN, M. G.

[Abstract] Since many data on hydrolysis of the title compounds are contradictory, the author sought to present principles that permit accurate quantitative analysis of reactivity in relation to structure. He discusses the effects of changing from methyl to ethyl and propyl radicals on the rate of aqueous or alkaline hydrolysis. The principles are consistent for either type, as well as for hydrolysis of esters of methylphosphonic acid, with the rate of hydrolysis at 90°C for dipropyl ester at 1.21 times that of dibutyl ester in either aqueous or alkaline variants. It was concluded that correlation of substituent effects on rate of hydrolysis of acid halides and esters of phosphoric, phosphonic and phosphonous acids were consistent and did not depend on the substituted group of the organic phosphorus compound. References 10: 9 Russian, 1 Western.
[105-12131]

UDC 547.341

REACTION OF UNSATURATED DIBROMOPHOSPHINES WITH ACETYLENE ALCOHOLS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 13 Apr 82) pp 2472-2476

BELYAYEVA, T. N., SENDYUREV, M. V., DOGADINA, A. V., IONIN, B. I. and PETROV, A. A., Leningrad Technological Institute imeni Lenosvet

[Abstract] Expanding previous research on the synthesis of highly unsaturated organophosphorus compounds, the authors studied reactions of dibromoanhydrides of alkene- and 2-bromoalkene phosphonous acids with primary and tertiary acetyl alcohols. Results showed formation of monoalkinyl esters of alkenyl(1,2-alkadienyl)phosphonic acids. Where voluminous substituents such as phenyl were present in the alpha position, allene phosphonic acids formed, while in the presence of mineral acids, the latter underwent cyclization to oxaphosphenes. Esters obtained using 3-methyl-1-butene-3-ol (Favorskiy alcohol) readily decomposed with low heating into corresponding phosphonic

acids. Biological tests showed that some oxaphospholenes possessed mild fungicidal properties. Chemical procedures are summarized in the experimental section. Figures 2; references 8: 5 Russian, 3 Western.
[105-12131]

UDC 547.558.1

REACTION OF TETRAETHYLAMIDES OF PHENYLPHOSPHONOUS AND PHENYLPHOSPHOROUS ACIDS WITH PRIMARY AROMATIC AMINES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 2 Jan 82) pp 2476-2481

TRISHIN, Yu. G. and CHISTOKLETOV, V. N., Leningrad Technological Institute for Cellulose and Paper Production

[Abstract] Previously the authors showed that trivalent phosphorus compounds with 2 chlorine atoms as substituents reacted with primary aromatic amines to form structures that varied depending on the nature of the third substituent (this journal, 1974 p 2590, 1979 p 48, 1975 p 1749). The present study considered such reactions where 2 dialkylamide groups accompanied a phenyl or phenoxy-group and beta-elimination was a further variable. Results showed that the reaction was one of transamidation of both diethylamine groups with formation of dianilides of phenylphosphonous acid. Structures were confirmed by infrared and ^{31}P NMR spectra. The reaction rate of tetraalkyldiamides of arylphosphonous acids with primary aromatic amines was in direct correlation to the basicity of the arylamine used. At the end of the reaction the mixture contained not only dianilides of phenylphosphorous acid, but also anilides of diphenylphosphorous acid and trianilides of phosphorous acid. The reaction was complicated by disproportions in initial and intermediate P^{III} compounds. Chemical procedures are summarized in the experimental section. References 9: 6 Russian, 3 Western.
[105-12131]

UDC 547.26'118

DERIVATIVES OF S-[(O-PHENYL-O-ALKYLDITHIOPHOSPHORYL)ACETYL]-THIOGLYCOLIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 16 Nov 81) pp 2481-2486

BELOVA, L. A., MANDEL'BAUM, Ya. A., SOYFER, R. S. and KOROLEVA, T. I.,
All-Union Scientific Research Institute for Chemical Means of Plant Protection, Moscow

[Abstract] Recently, esters and amides of the title acids were shown to have a significant biocidal activity ((this journal, 1981 p 1982, NOVYE KHIMICHESKIYE SREDSTVA ZASHCHITY RASTENIY (miscellany), 1979 p 23)). The present study

presents results of substitution reactions with chlorine atoms in higher chlorocyclophosphazenes reacting with amines and phenolates in such syntheses as that of ammonolysis of phosphorus pentachloride by ammonium chloride in a chlorobenzene medium in the presence of quinoline as a catalyst, and synthesis of arylhydroxy-derivatives of higher cyclical phosphazenes with sodium phenolate in TGF. PMR and elemental analysis confirmed the structures of the resulting compounds. Where these chlorophosphazenes were used for a reaction with butylamine, only a single substituted heptamer formed, making possible a directed synthesis of derivatives of this homolog, which proved to be the most desirable compound from a thermodynamic point of view. Introduction of pentamers and lower homologs violated the order of regrouping. Thus the regrouping principles depended on the composition of the initial mixture of cyclical chlorophosphazenes and on the type of nucleophile employed.

Figures 4; references 4 (Russian).

[105-12131]

UDC 546.18

REACTION OF RING REGROUPING IN PROCESSES OF NUCLEOPHILE SUBSTITUTION IN CHLOROCYCLOPHOSPHAZENES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 2 Nov 81) pp 2486-2491

MITROPOL'SKAYA, G. I., KIREYEV, V. V., KORSHAK, V. V. and GORYAYEV, A. A.,
Moscow Chemical and Technological Institute imeni D. I. Mendeleyev

[Abstract] The authors previously discovered changes in ring dimensions in processes of division, polymerization and substitution of the chlorine atoms as ring dimensions varied (DOKLADY AN SSSR, 1978 p 853). The present study gives results of study of chlorine atom substitution in higher chlorocyclophosphazenes $(NPCl)_n$, where $n \geq 5$, in reaction with amines and phenolates. Synthesis of arylhydroxy-derivatives of higher cyclical phosphazenes was accomplished through the reaction of sodium phenolate in TGF medium. Element analysis and PMR spectroscopy were used to confirm structures, and ^{31}P NMR showed the presence of substances with singlet values at +4.5, +5.6 and +16.8. Use of a balanced mixture of dodeca(butylamino)cyclohexaphosphazene and the corresponding heptamer made it possible to conduct a directed synthesis to obtain the compound that was thermodynamically most desirable. Use, for reactions with sodium phenolate, of a mixture containing penta-, hexa- and heptamers permitted conducting the reaction with a regular change in composition in the direction of increasing the relative quantity of rings with lesser dimensions. With aminolysis, lower homologs could disappear, i.e., the initial mixture could contain 5 cycles, while the product of substitution had 3 compounds. Patterns of regrouping are determined by the composition of the initial mixture of cyclic chlorophosphazenes, as well as by the type of nucleophile used. Figures 4; references 4 (Russian).

[105-12131]

PHOSPHORYLATION OF N,N-DISUBSTITUTED AMIDES WITH PHOSPHORUS PENTACHLORIDE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82

(manuscript received 7 Jul 81) pp 2491-2499

PENSIONEROVA, G. A., ROZINOV, V. G., KALABINA, A. V., DONSIKII, V. I.,
 RATOVSKIY, G. V. and DMITRICHENKO, M. Yu., Irkutsk State University
 imeni A. A. Zhdanov; Institute of Petroleum- and Coal Chemistry Synthesis,
 Irkutsk State University

[Abstract] The authors previously established that tertiary amines react with phosphorus pentachloride forming enamines containing phosphorus, but the reaction was complicated by side processes and tarring due to the high nucleophilicity of the amines. The title phosphorylation had not previously been reported; the authors determined that at room temperature the reaction of N,N-disubstituted amides with PCl_5 in a benzene solution led to products of $[\text{R}_2\text{N}=\text{C}(\text{Cl})\text{R}]+\text{PCl}_6^-$. Structures obtained were confirmed by ^{31}P NMR and ^{31}P NMR, infrared and chemical analysis. The authors also conducted tests to confirm the identical nature of the compounds synthesized with Wilsmeier reagents. Products of the reaction of the amides with phosphorus oxychloride had the structure $[\text{R}_2\text{N}=\text{C}(\text{Cl})\text{R}]^+\text{OPOCl}_2$. The reaction appeared to begin with an attack on the carbonyl oxygen by PCl_5 , after which the nature of the substituent, reagent ratios and temperature determined further features. In contrast to ketones and complex esters the tested amides tended to promote formation of azomethine groupings. The process could be directed toward phosphorylation and formation of a double carbon-carbon bond if electron acceptor substituents were added to the nitrogen. Chemical procedures are summarized in the experimental section. Figures 2; references 9: 3 Russian, 6 Western.

[105-12131]

UDC 547.118:541.128:542.938

CATALYSIS BY AMINES OF HYDROLYSIS OF DI(p-NITROPHENYL)METHYLPHOSPHONATE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82

(manuscript received 11 Jan 82) pp 2503-2507

BAKEYEVA, R. F., KUDRYAVTSEVA, L. A., FEDOROV, S. B., BEL'SKIY, V. Ye. and
 IVANOV, B. Ye., Institute of Organic and Physical Chemistry
 imeni A. Ye. Arbuzov, Kazan Branch, USSR Academy of Sciences

[Abstract] Despite earlier studies, predicting catalytic activity of amines remains incompletely examined. The authors studied various primary, secondary and tertiary amines to clarify the effect of structure on catalytic activity. Using diethylenetriamine it was learned that the rate of substrate hydrolysis depended on the concentration of amine, hydroxyl

ions and water (Brass and Bender, Journal of the American Chemical Society, 1972 p 7421). The authors found that parameters for Bronsted equations actually depended on the number of NH bonds in the amines tested. Rates for neutral and monoprotic-types of ethylenediamine and DETA were connected to solution pH and its effect on the rate of hydrolysis of the substrate in the presence of given amines, while activation energy depended on amine structure. If catalysis by some nucleophile mechanism took place, it could lead to formation of products of aminolysis in reactions catalyzed by primary and secondary amines. Chemical procedures are summarized in the experimental section. Figures 1; references 9: 4 Russian, 5 Western.
[105-12131]

UDC 547.26'118

HYDRAZIDES OF S-[(O,O-DIALKYLDITHIOPHOSPHORYL)ACYL]THIOGLYCOLIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 22 Feb 82) pp 2507-2512

BELOVA, L. A., MANDEL'BAUM, Ya. A., SOYFER, R. S. and KOROLEVA, T. I.,
All-Union Scientific Research Institute for Chemical Means of Plant
Protection, Moscow

[Abstract] Esters and amides of the title compound have significant biocidal activity, and hydrazides of phosphorylalkylcarboxylic acids are strong pesticides. The authors sought to synthesize pesticides using hydrazides of the title compounds. Several side reactions occurred, producing among other things N,N'-bis(O,O-dialkyldithiophosphorylacyl)hydrazides, a dihydrazide of dithiodiglycolic acid and salts of dialkyldithiophosphorylalkylcarboxylic acids with dihydrazide of dithioglycolic acid. Causes for such products and infrared and PMR spectra used to confirm their structure are discussed. Biological tests showed that the compounds obtained are contact insecto-acaricides, but are not as effective as methaphos, used as the standard for comparison. Chemical and spectral information is given in the experimental section. References 9: 3 Russian, 6 Western.
[105-12131]

OSCILLATING SPECTRA AND STRUCTURE OF BIS(TRICHLOROMETHYL)TRICHLOROPHOSPHORANE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 30 Dec 81) pp 2513-2516

KOZLOV, E. S., BOLDESKUL, I. Ye., KARMANOV, V. I., KOZULIN, A. T.,
KYUNTSEL', I. A., MOKEYEVA, V. A. and SOYFER, G. B., Institute of Organic
Chemistry, UkSSR Academy of Sciences, Kiev

[Abstract] Spectral data of nuclear quadruple resonance show the title compound has the structure of a trigonal dipyramid with CCl_3 groups in axial positions, with significant intramolecular spatial reactions that limit mobility. Spectral data of ^{31}P NMR indicate that the pentacoordinated structure of the compound is maintained in benzene, nitrobenzene and nitromethane, but other geometrical factors were unclear and this led to the present study, using oscillating spectroscopy, of solid forms at 298 and 133K and in a benzene solution. Infrared spectra were also studied. The nature of spectra for solid state and dissolved forms were identical. Absorption of low-frequency waves resulted from librational and translational oscillations of molecules in the crystalline matrix; these factors were considered in reaching a preliminary conclusion that the force constant of the P-Cl bond of $(\text{CCl}_3)_2\text{PCl}_3$ phosphorane was less than that of the corresponding CCl_3PCl_4 due to lesser negative charge of the axial substituents. References 8: 7 Russian, 1 Western.
[105-12131]

PROPERTIES OF DIAMIDOBROMOPHOSPHAZOALKANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 12 Jan 82) pp 2517-2526

MIROSHNICHENKO, V. V., MARCHENKO, A. P., KUDRYAVTSEV, A. A. and
PINCHUK, A. M., Institute of Organic Chemistry, UkSSR Academy of Sciences,
Kiev

[Abstract] The title compounds had received little attention until the authors' procedure for their synthesis and study was developed (this journal, 1980 p 951). The process involves thermal decomposition of triamidobromophosphonium bromides, in which attachment of hydrochlorides leads to formation of hydrobromide salts of chlorophosphazoalkanes, and, subsequently, the chlorophosphazoalkanes themselves. Details of structure obtained from ^{31}P NMR are presented. Thermal decomposition tests showed that with heating of such compounds the bromine anion attacks not only the substituent at the nitrogen atom, but also the phosphorus atom. Where alkanes containing chlorine have nucleophile properties, the tested compounds

containing bromine more typically had electrophile properties. Reaction capability also differed between compounds with chlorine and those with bromine with clearly opposite features appearing. The authors hypothesize that introduction of dialkylamide groups into trihalide phosphazoalkanes would result in a transition from nucleophilicity, highest with fluorine- and descending to the iodine-derivatives, and the opposite trend of rising electrophile tendency and capacity for polymer formation, lowest with fluorine- and rising to iodine-derivatives. Chemical procedures and spectral data are given in the experimental section. References 13: 9 Russian, 4 Western.
[105-12131]

UDC 547.26'118

ALKYLATION OF ALDEHYDES AND KETONES BY PENTA(alpha,alpha,omega-
TRIHIDROPOLYFLUOROALKOXY)PHOSPHORANES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 7 Dec 81) pp 2526-2531

SHERMOLOVICH, Yu. G., KOLESNIK, N. P., ROZHKOVA, Z. Z., KASHKIN, A. V.,
BAKHEUTOV, Yu. L. and MARKOVSKIY, L. N., Institute of Organic Chemistry,
UkSSR Academy of Sciences, Kiev

[Abstract] Preparative uses for phosphoranes have received attention recently for synthesizing heterocyclic compounds and as alkylating agents. The authors were among the first to study the title reactions. Results indicated that a mixture of paraform and phosphorane heated at 160-200°C for 7-9 hours yielded the title compound. Phosphoranes reacted with unsaturated aldehydes with hydrogen atoms in a trans-position to form only a trans-isomer of the alkylation product. Gas-liquid chromatography and PMR spectral data confirmed these findings. Acetylacetone in analogous conditions reacted to form vinyl esters rather than ketals, apparently due to isomerization of the cis-isomer that formed along with the trans-isomer, the former now becoming a thermally more-stable trans-isomer. Chemical procedures and spectral data are given in the experimental section. Paraform, aldehydes and ketones reacting with the title compounds all contained electron-acceptor substituents at the carbonyl group. The reaction of polyfluoroalkoxyphosphoranes with acetylacetone led to polyfluoroalkylvinyl groups, while with chloral haloform fission led to the formation of chloroform and polyfluoroalkylformiate. References 16: 6 Russian, 10 Western.
[105-12131]

REACTION OF 1- α -FURYL-2-NITROETHYLENE WITH TRIALKYLPHOSPHITES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 6 Feb 82) pp 2532-2539

VAFINA, N. M., YEFREMOV, Yu. Ya., ZYABLIKOVA, T. A., IL'YASOV, A. V. and
SHERMERGORN, I. M., Kazan Veterinary Institute imeni N. E. Bauman; Institute
of Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan

[Abstract] Study of esters of trivalent phosphorus acids in reaction with nitroolefins has shown that intermediate products are converted, in different directions, depending on the surroundings of the phosphorus atom, the nature of the nitroolefin and the medium. The authors studied the reaction of the title compound with phosphites in acetic acid since the mobility of hydrogen bound with the α -carbon atom of the bipolar ion is higher than in the adduct with beta-nitrostyrene due to higher electronegativity of the α -furan fragment compared to phenyl. Results showed that the reaction with trimethylphosphite was more energetic than that with beta-nitrostyrene. The dominant process of decomposition was dissociation at one of the P-C bonds. Mass, P.M.R, infrared and ^1H NMR spectra were registered to follow the course of decomposition and determine structures. The rate at which the intermediate product decomposed to 1- α -furylvinylphosphonate and alkylnitrite significantly surpassed its rate of protonization by acetic acid; side products included amides of dialkylphosphoric acids and/or dialkylphosphates of dialkyl- α -hydroxyalkylphosphonates. Chemical procedures and spectral data are given in the experimental section. Figures 1; references 14: 7 Russian, 7 Western.
[105-12131]

UDC 541.121:536.7:547.241

ASSOCIATION CONSTANTS OF PHENOL WITH ARYLDIMETHYL- AND DIARYLMETHYLPHOSPHINE OXIDES AND FEATURES OF TRANSMISSION OF ELECTRONIC EFFECTS IN MOLECULES OF ORGANOPHOSPHORUS COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 29 Mar 82) pp 2636-2637

DOROKHOVA, N. I., SHVETS, A. A., GONCHAROVA, L. V. and OSIPOV, O. A.,
Rostov State University imeni M. A. Suslov

[Abstract] Infrared spectroscopy was used to determine association constants of phenol with two groups of phosphine oxides. The electron nature of the substituent led to variations in the parameter from $2 \cdot 10^3$ to $3 \cdot 10^2$ mol/l. The association of phenol with triarylphosphine oxides pointed out the key role of linking in these compounds. The aromatic ring and the phosphoryl

group in all phosphine oxides were acoplanar, but increasing the acoplanar level of molecules did not obstruct increases in linking. Increased linking in aromatic oxides accompanying increasing numbers of aromatic groups bound to the phosphorus atom was also noted in studying infrared spectral parameters of H-complexes of phosphine oxides. References 4 (Russian).
[105-12131]

UDC 547.241

INVERSION OF REGIOSPECIFICITY IN REACTIONS OF 1,3-DIPOLAR CYCLOADDITION OF DIAZOALKANES TO beta-CARBOMETHOXYVINYLPHOSPHORYL COMPOUNDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 15 Feb 82) pp 2637-2638

GAREYEV, R. D. and PUDOVIK, A. N., Kazan Veterinary Institute
imeni N. E. Bauman

[Abstract] The reaction of 1,3-dipolar cycloaddition of diazomethane to beta-carbomethoxyvinylphosphonates leads to mixture of 3- and 4-phosphorylated Δ^2 -pyrazolines, with the latter predominating. This and inverse results with 2-diazopropane led the authors to seek a dipolarophile system with a chiral phosphorus atom that would give Δ^2 -pyrazolines with alternative orientation of the diazo-component allowing assessment of stereospecificity of 1,3-dipolar cycloaddition as a function of the regiospecificity of the reaction. The system identified was O-methylmethyl-beta-carbomethoxyvinylphosphinate. Along with spatial reactions, the electron nature of substituents in the reaction center of both partners to cycloaddition played an important role. References 1 (Russian).
[105-12131]

UDC 547.341.26'118.07

SYNTHESIS OF beta,gamma-PHOSPHORYLATED KETONES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 29 Mar 82) pp 2639-2640

BREL', A. K. and RAKHIMOV, A. I., Volgograd Polytechnical Institute;
Volgograd Medical Institute

[Abstract] Arbuzov reactions used to obtain phosphorylated ketones, particularly gamma-types, have low yields. The authors developed a simple and practical method for their synthesis by homolytic addition of aliphatic aldehydes to vinyl- or allylphosphonates. Acyl peroxides were used for initiation with temperatures of decomposition that corresponded to reaction temperatures. Selectivity was good, but with readily polymerizing

vinylphosphonate, telomerization complicated the process. Product purity was confirmed by thin layer chromatography. References 3 (Western).
[105-12131]

UDC 547.241

STUDY OF PRODUCTS OF OXIDIZING PHOSPHORYLATION OF PYRIDINE BY ^{31}P NMR METHOD

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 19 Apr 82) pp 2640-2641

AKHLEBININ, A. K., BORISOV, Ye. V. and NIFANT'YEV, E. Ye., Moscow State Pedagogical Institute imeni V. I. Lenin

[Abstract] N-phosponium salts of pyridine containing macroergic P-N bonds have wide use in synthesizing polypeptides, polyamides and polyurethanes. While analysis of chemical conversions and infrared spectra provided some information on the process, the authors assert that ^{31}P NMR spectra permit considerably more precise description of the composition of the products and the impact of synthesizing conditions on it. References 2 (Western).
[105-12131]

UDC 547.241

PHOSPHORYLATION OF N-AMINOPYRIDINE

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 19 Apr 82) pp 2641-2642

BORISOV, Ye. V., AKHLEBININ, A. K. and NIFANT'YEV, E. Ye., Moscow State Pedagogical Institute imeni V. I. Lenin

[Abstract] Continuing their earlier study of mesoionic compounds with P-N bonds (this journal, 1982 p 218, p 2640), the authors examined phosphorylated derivatives of N-aminopyridine and determined that the effect of chlorophosphite on equimolar amounts of its iodide in benzene or acetonitrile in the presence of triethylamine was to form N-(4-methyl-2-imido-1,3,2-dioxaphosphorinano)pyridine. In 24 hours the ^{31}P NMR spectrum showed no initial 4-methyl-2-chloro-1,3,2-dioxaphosphorine. Addition of excess sulfur and heating to 60°C for 10 minutes brought formation of N-(4-methyl-2-imido-2-thio-1,3,2-dioxaphosphorinano)pyridine. References 4: 2 Russian, 2 Western.
[105-12131]

TRANSAMIDATION REACTION IN SYNTHESIS OF METHYLENEAMIDOPHOSPHITES AND
N₆-PHOSPHORYLATED SIDNONIMINES; NEW PHOSPHORANE INTERMEDIATE; CONFIGURATION
OF SUBSTITUENTS AT PHOSPHORUS ATOM

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 19 Apr 82) pp 2642-2644

BORISOV, Ye. V., AKHLEBININ, A. K., BORISENKO, A. A. and NIFANT'YEV, E. Ye.,
Moscow State Pedagogical Institute imeni V. I. Lenin; Moscow State
University imeni M. V. Lomonosov

[Abstract] Seeking successful methods for synthesizing compounds with the
fragment C=N-P(X), the authors tested phosphorylation of phosphorous acid
by amidoesters. One day after mixing freshly distilled 4-methyl-2-dimethyl-
amido-1,3,2-dioxaphosphorinane with equimolar quantities of diphenylketimine,
31P NMR spectra indicated the presence of a trans-isomer of this compound,
previously synthesized by another method. Attempted reverse reaction failed.
The reduction of signals from 4 to 2 in a related amide, a neopentylene de-
rivative, is related to the latter's great mobility and the syn-anti-
isomerism of amide data. Chemical procedures are summarized. References 7:
5 Russian, 2 Western.

[105-12131]

UDC 547.241'64

REGULATING DIRECTION OF HYDROPHOSPHORYLATION OF CYCLOOLIGOENES

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 30 Mar 82) pp 2644-2645

MASLENNIKOVA, V. I., MACDEYEVA, R. K., ZYK, N. V. and NIFANT'YEV, E. Ye.,
Moscow State Pedagogical Institute imeni V. I. Lenin

[Abstract] Data indicate that homolytic addition of dialkylphosphites to
cyclooligoenes takes place either through opening of a double bond or by a
route that combines hydrophosphorylation with intramolecular cyclization.
Since no studies analyzing this contradiction have been published, the
authors studied such phenomena with cis,cis-cyclooctadiene, and cis,trans-
trans-cyclododecatriene in the presence of peroxides, and determined that
in traditional circumstances addition is always combined with exhaustive
cyclization. With strong acids such as trichloroacetic acid, a mixture
of products with unsaturated organic phosphorus substances results,
apparently as a result of blocking of part of the short bonds in the
cyclooligoenes. References 3: 1 Russian, 2 Western.

[105-12131]

REACTION OF DIALKOXYPHOSPHORYLISOCYANATES WITH CARBOXYLIC ACIDS

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 15 Mar 82) pp 2645-2646

NIKONOROV, K. V., LATYPOV, Z. Ya. and ANTOKHINA, L. A., Institute of
Organic and Physical Chemistry imeni A. Ye. Arbuzov, Kazan Branch,
USSR Academy of Sciences

[Abstract] Organic isocyanates are known to react with aliphatic and aromatic carboxylic acids, releasing CO₂ and forming either the acid's amide or symmetrical disubstituted ureas. The title isocyanates, however, do not react with benzoic acid; they react with acetic and propionic acids only in the presence of catalytic quantities of sulfuric acid, releasing CO₂ and forming the phosphorylated amide of carboxylic acid. The reaction passed through an unstable intermediate stage. Chemical procedures are summarized. References 4: 2 Russian, 2 Western.
[105-12131]

REACTION OF AMIDES OF DIIMIDOPHOSPHENYLIC ACID WITH TRIMETHYLALUMINUM

Leningrad ZHURNAL OBSHCHEY KHIMII in Russian Vol 52, No 11, Nov 82
(manuscript received 30 Mar 82) pp 2648-2650

ROMANENKO, V. D., SHUL'GIN, V. F., BRUSILOVETS, A. I., SKOPENKO, V. V. and
MURKOVSKIY, L. N., Institute of Organic Chemistry, UkSSR Academy of Sciences

[Abstract] Synthesis and structural study of four-member rings containing phosphorus and nitrogen in combination with chelated metal atoms have recently received much attention. The authors describe the first example of the reaction of sigma³lambda⁵-phosphorazailides with alkyl metal derivatives. It was determined that trimethylaluminum at 20° C in benzene readily attached to amides of diimidophosphenylic acid forming coordinated compounds, which are diagrammed. Chemical procedures and NMR spectral data are given. References 5 (Western).
[105-12131]

EFFECT OF ELECTRON AND SPATIAL FACTORS ON STRUCTURE OF SUBSTITUTED AMIDES OF TRIVALENT PHOSPHORUS ACIDS

Moscow VESTNIK MOSKOVSKOGO UNIVERSITETA, SERIYA 2: KHIMIYA in Russian
Vol 23, No 6, Nov-Dec 82 (manuscript received 2 Jul 82) pp 593-605

LUTSENKO, I. F., FOSS, V. L., VEYTS, Yu. A. and CHERNYKH, T. Ye., Department of Organic Chemistry, Moscow State University imeni M. V. Lomonosov

[Abstract] Relative thermodynamic stability of isomeric compounds with three- or four-coordinated phosphorus atoms depends not only on other elements contained but also on the nature of the substituents. The authors review literature data and present their own research on the title factors, for amides of phosphonous and phosphorous acids, determining that the electron properties of the substituent at the nitrogen atom was the most influential, and for element-substituted amides of phosphonous acids with Si, Ge, Sn, As or Sb, determining by infrared, PMR and ^{31}P NMR in particular that the nature of the Al, Ar, OAl or NAl substituent was the key determinant. With moderate spatial obstacles in the molecule, balance was skewed in the direction of a compound with a three-coordinated phosphorus atom, but where $\text{R}=\text{t-Bu}$, both isomers had comparable stability. Where the acceptor substituent was PR_2 , as for SiMe_3 , isomer stability became comparable with secondary radicals at the phosphorus atom. The growth of four-coordinated phosphorus atoms was considered to be connected to high sensitivity to increased spatial obstructions in the smaller dyad center. The authors were able to identify several new groupings including the first examples of germano- and stannotropy of dyad systems. References 37: 17 Russian, 20 Western.
[126-12131]

UDC 542.97:547.1'118

CATALYTIC PHOSPHORYLATION OF POLYFLUOROALKANOLS, REPORT 9: PHOSPHORYLATION OF 1,1-DIHYDROFLUOROALKANOLS IN PRESENCE OF CHLORIDES OF METALS OF THE FIRST GROUP OF THE PERIODIC SYSTEM

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 11, Nov 82 (manuscript received 26 Apr 82) pp 2535-2540

KUDRYAVTSEV, I. Yu., ZAKHAROV, L. S. and KABACHNIK, M. I., Institute of Heteroorganic Compounds imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] The authors have shown earlier that metal salts, especially salts of the metals of the second group of the periodic system are effective catalysts for the title phosphorylation by chloranhydrides of pentavalent phosphorus acids. Metals of the first group had received little attention, so the authors studied them in reaction with 1,1-dihydroperfluorobutanol and

phosphorus oxychloride, heated to 160° C. Results showed relative catalytic activity to descend in the order $\text{LiCl} > \text{RbCl} > \text{CsCl} > \text{NaCl} > \text{KCl}$. LiCl was found to be the equal of magnesium in this regard, and was considered to be a useful catalyst for producing corresponding diaryl(polyfluoroalkyl)phosphates with good yields. References 5 (Russian).
[106-12131]

UDC: 546.18+547.315.1

INTERACTION OF TRIPHENYL-3-PHENYL-1,2-PROPADIENYL⁺PHOSPHONIUM BROMIDE WITH
HYDRAZINE HYDRATE

Yerevan AR'YANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 35, No 11, Nov 82
(manuscript received 12 Mar 82) pp 761-762

KHACHATRYAN, R. A., MKRTCHYAN, G. A., ZALINYAN, S. A. and INDZHIKYAN, M. G.,
Institute of Organic Chemistry, Armenian Academy of Sciences, Yerevan

[Abstract] Continuing previous work, a study was made of the interaction of triphenyl-3-phenyl-1,2-propadienylphosphonium bromide with hydrazine hydrate. It is shown that the reaction in benzene solution is exothermic at room temperature, leading to the formation of triphenylphosphine oxide and methylbenzylketone azine with near quantitative yield. The most probable reaction mechanism is selected on the basis of a study of the interaction of methylbenzylketone with hydrazine hydrate. References 3: 2 Russian, 1 Western.
[133-6508]

UDC 622.276.1

EFFECT OF CONCENTRATED ALKALI SOLUTIONS ON COUNTERFLOW CAPILLARY EXTRACTION OF PETROLEUM BY WATER AT HIGH TEMPERATURES

Baku DOKLADY AKADEMII NAUK AZERBAYDZHANSKOY SSR in Russian Vol 38, No 7, Jul 82 (manuscript received 16 Jul 80) pp 60-63

TAIROV, N. D., VEZIROV, D. Sh., KERIMOVA, F. G. and BARYAKINA, M. A.,
Institute of Problems of Deep Oil and Gas Deposits (presented by
Academician M. T. Abbasov, AzSSR Academy of Sciences

[Abstract] Earlier theoretical and experimental research has shown that extracting petroleum from heterogeneous hydrophilic rocks can be aided by natural capillary action. The authors studied, under laboratory conditions, the effectiveness of assisting this process by adding NaOH to scrub and force out crude oil, and increasing temperature to determine its effect. Using glass columns 40 cm X 3 cm filled with hydrophilic quartz sand, they determined that temperature had a significant effect on counterflow capillary extraction of oil by alkalis. Temperature increases speeded the separation of the petroleum film from rock surfaces, thus improving the degree of capillary action. Figures 3; references 6: 5 Russian, 1 Western.
[102-12131]

UDC 615.241:582.892].015.35

SAFETY IN USING PREPARATION OF GINSENG PLANT TISSUE BIOMASS IN EXPERIMENTS

Moscow FARMATSIYA in Russian Vol 31, No 6, Nov-Dec 82
(manuscript received 10 Jul 80) pp 45-49

KRENDAL', F. P., KUDRIN, A. N., LEVINA, L. V., CHUBAREV, V. N.,
ALEKSANDROVA, I. V., DANILINA, A. N., SOKOLOV, I. K., KAPLAN, E. Ya.,
FRIDMAN, Ya. S. and ZEL'TSER, P. L., First Moscow Medical Institute
imeni I. M. Sechenov

[Abstract] Study of toxicological, biochemical, hematological and histomorphological aspects of ginseng tissue use was made in steps of comparative acute toxicity, determination of chronic toxicity, and study of local irritant action. Analysis of results of these tests made on laboratory white mice and rats, including effects on the respiratory and circulatory systems, blood, liver, kidneys and other indicators showed no ill effects compared to control groups. Some increase in alanine aminotransferase bore witness to dystrophic shifts in histomorphological cellular elements with extremely high doses. Blood glucose declined somewhat. Histological study of internal organs showed no noticeable changes.

References 3 (Russian).

[101-12131]

UDC 615.014.47:661.185

EFFECT OF SOLVENTS ON SURFACE ACTIVE COLLOIDO-MICELLAR AND FOAM-FORMING PROPERTIES OF TWEEN-80

Moscow FARMATSIYA in Russian Vol 31, No 6, Nov-Dec 82
(manuscript received 2 Dec 81) pp 37-39

DIL'BARKHANOV, R. D., LYAPUNOV, N. A., CHUYESHOV, V. I., BASHURA, A. G.,
LYAPINOVA, O. Ya. and BASHIKOVA, G. Kh., Kharkov Pharmaceutical Institute

[Abstract] The authors studied the effects of DMSO, propylene glycol, polyethylene glycol 400 molecular weight, (PEG-400) triethylene glycol,

DMFA, ethanol and isopropanol on surface tension, critical concentrations of micellar formation of Tween-80 and the stability of foams treated with it. If the surface tension of the tested solvent was less than that of water, as in ethanol and isopropanol, its 5-10% addition to water reduced surface tension markedly, while further additions of the solvent had little additional effect. A second group of solvents, including DMSO showed a linear effect on surface tension as its quantity was increased. Yet a third group, including 400 polyethylene glycol, triethylene glycol and DMFA, had an intermediate effect. Results showed increased critical concentrations of micellar formation and decreased foam stability for all but ethanol, isopropanol and propylene glycol, which in concentrations of 25, 15 and 15%, respectively, increased the life of foam stabilized by Tween-80. Figures 4; references 6: 5 Russian, 1 Western.

[101-12131]

POLYMERS AND POLYMERIZATION

UDC 541.138.3:547

STUDY OF ELECTROCHEMICAL POLYMERIZATION OF ACRYLAMIDE IN AQUEOUS SOLUTIONS CONTAINING ALUMINUM CHLORIDE

Moscow ELEKTROKHIMIYA in Russian Vol 18, No 12, Dec 82
(manuscript received 12 Feb 81; after revision 23 Oct 81) pp 1656-1659

TIKHONOVA, L. S., MAKAROV, K. A., ZYTNER, Ya. D. and SOKOLOVA, L. A.,
Leningrad Technological Institute imeni Lensovet

[Abstract] Electrochemically-initiated copolymerization has promise for producing hydrogel polymer coatings of polyacrylamide, which is useful due to its thrombo-resistant properties. Such coatings produced by electrolysis have the shortcoming of high zinc content. The authors therefore turned to aluminum chloride because its high chemical activity precludes it from forming aluminum deposits on electrodes. Results with the test electrode were compared to a control test using a silver chloride electrode. Tests with the aluminum chloride and mercury drop, solid nickel and copper electrodes helped to clarify the reactions. The initiator of polymerization came with the first wave of current and anion particles formed in the electrode layer as the aluminum was separated from the adsorption complex. Figures 4; references 7: 4 Russian, 3 Western.

[108-12131]

UDC 541.15:547.413:546.16

RADIATIONAL CHEMICAL CONVERSIONS OF FLUORO-OLEFINS

Moscow IZVESTIYA AKADEMII NAUK SSSR: SERIYA KHIMICHESKAYA in Russian No 11, Nov 82 (manuscript received 19 Mar 82) pp 2452-2457

FOVIN, A. V. and VOLKOVA, Ye. V., Institute of Heteroorganic Compounds
imeni A. N. Nesmeyanov, USSR Academy of Sciences, Moscow

[Abstract] Advantages of polymerization of the title compounds include the absence of any required chemical initiator, low temperature initiation,

polymerization in the solid phase and, in some cases, polymerization of otherwise hard-to-polymerize monomers. To further define the chemical behavior of this class of compounds, the authors studied radiolysis of fluoro-olefins, homopolymerization, copolymerization and grafting polymerization of tetrafluoroethylene, trifluorochloroethylene, trifluoroethylene, fluorine vinylidene and fluorine vinyl. The first of these was studied most thoroughly in gaseous and liquid phases with excess monomer pressure, and it was shown to polymerize readily under beta- and gamma radiation. Hexafluoropropylene polymerized at much slower rates, while perfluoroisobutylene showed little change despite prolonged 250 Mrad radiation at 600 rad/sec. The slowest of tested compounds to form polymers was ethylene. The nature of the double bond and reactivity in radical polymerization, which increases from ethylene to tetrafluoroethylene, are discussed. Further research focused on kinetics of grafting of fluoroethylene and ethylene to polytetrafluoroethylene that had previously been irradiated in helium at $0.72 \cdot 10^6$ rad. Results correlated with those for homopolymerization of these compounds. In general, results indicated that in radiolysis and photolysis the decay of TFE molecules occurs at the double bond, with formation of difluorocarbene. The rate of radiational polymerization descends in the following order:

$\text{CF}_2=\text{CF}_2 > \text{CF}_2=\text{CFH} > \text{CF}_2=\text{CH}_2 > \text{CFH}=\text{CH}_2 > \text{CH}_2=\text{CH}_2$. References 38: 33 Russian, 5 Western.

[106-12131]

UDC 541.64:539.124.6

STUDY OF OXIDIZED POLYMERS BY POSITRON ANNIHILATION METHOD

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 24, No 12, Dec 82
(manuscript received 15 Jul 81) pp 2579-2583

ONISHCHUK, V. A., PUDOV, V. S., SHANTAROVICH, V. P. and YASINA, L. L.,
Institute of Chemical Physics, USSR Academy of Sciences

[Abstract] Positron methodology has been used to study electron structure and microdefects in condensed-state substances. In the present study the authors seek to apply it to learn about oxidation of amorphous and crystalline specimens of poly-4-methylpentene-1 oxidized at various temperatures between 120 and 160°C. Data was processed according to the hypotheses that positrons form in a quasi-free state and can then be trapped by any defect; defects forming during oxidation can inhibit positrons by restraining electrons and by reducing their general mobility; in amorphous areas there is a tunneling effect that directs positrons to larger defects; and diffusion between amorphous and crystalline structures can be disregarded. Results indicated that at 120°C there was practically no oxidation in crystalline areas of the polymer, while at 160°C it was pronounced and could be described by the dependence of intensity on the temperature. A phase transition was noted between 140-150°C. Activation energy for amorphous areas was 99.0 ± 4.6 , while crystalline areas it was 183.1 ± 12.4 kJ/mol. Figures 2; references 14: 5 Russian, 9 Western.

[112-12131]

MECHANISM OF REACTIONS INHIBITED BY THERMAL DECOMPOSITION OF BENZOYL PEROXIDE IN POLYAMIDE

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 24, No 12, Dec 82
(manuscript received 20 Jul 81) pp 2601-2608

MAKAROV, G. G., MIKHEYEV, Yu. A., PARIYSKIY, G. B., POSTNIKOV, L. M.
and TOPTYGIN, D. Ya., Institute of Chemical Physics, USSR Academy of Sciences

[Abstract] In earlier reports the authors discussed macroscopic stages of the title decomposition (this journal, 1982 pp 618, 1246). In this article they report on the effects of oxygen and 2,6-di-tert-butyl-4-methylphenol (DTBMP), and 2,4,6-tri-tert-butylphenol (TTBP) on the destruction and decomposition of the initiator, thus permitting more precise determination of the reaction mechanism both in an inert atmosphere and in oxygen. Hypothesizing that hydroperoxides are consumed in secondary processes, the authors describe the rate of benzoyl peroxide consumption in polyamide in an inert atmosphere, the difference when oxygen is the medium, when DTBMP practically completely prevents breakdown of polyamide macromolecules, and breakdown of such chains in an inert atmosphere. Four types of macroradicals were noted, of which only one caused benzoyl peroxide to decompose. This compound was thought to react with an unsaturated molecule formed in a macroradical decomposition. Breakdown of polyamide macromolecules is related to the earliest stages of initiated conversions, when formation of P_1 and P_1O_2 macroradicals is "fatal" for it. Figures 3; references 9: 4 Russian, 5 Western.

[112-12131]

UDC 541(64+127):539.839:547.322

KINETIC FEATURES OF POLYMERIZATION OF 1,1,2,3-TETRACHLOROBUTADIENE-1,3 UNDER HIGH PRESSURE

Moscow VYSOKOMOLEKULYARNYYE SOYEDINENIYA in Russian Vol 24, No 12, Dec 82
(manuscript received 22 Jul 81) pp 2621-2627

ZHULIN, V. M., MAKAROVA, Z. G., KLIMENTOVA, N. V., SUPRUN, A. P.,
AKOPYAN, A. N. and SHAKHOVSKOY, G. P., Institute of Organic Chemistry
imeni N. D. Zelinskiy, USSR Academy of Sciences; Institute of Heteroorganic
Compounds imeni A. N. Nesmayanov, USSR Academy of Sciences

[Abstract] Previously similar compounds had been shown to form high-molecular compounds only under high pressure; such polymerization had an anomalous nature and quantitative information was insufficient to explain it. The current study seeks to provide more precise information based on the example of the title compound (TCB), using methylmethacrylate and styrene as the monomers. Results indicated that polymerization was speeded as pressure

increased, as expected, but with diminishing increase rate at higher pressures. This seemed to indicate that the reaction took place under conditions close to those of the monomer's crystallization. Further observations of pressure, polymerization and crystallization tended to confirm this hypothesis, and led to the conclusion that rapid polymerization of TCB occurs in the area of the phase transition from liquid to solid state, with polymerization and crystallization as competing processes. This occurred with both MMA and styrene monomers. At atmospheric temperature essentially no polymerization took place. Figures 4; references 19: 13 Russian, 6 Western.
[112-12131]

UDC: 542.952.6+678.046+678.744.422

POLYMERIZATION FILLING OF POLYVINYL ACETATE WITH PERLITE

Yerevan ARMYANSKIY KHIMICHESKIY ZHURNAL in Russian Vol 35, No 11, Nov 82
(manuscript received 25 Dec 81) pp 754-757

AKOPYAN, L. A., POKRIKYAN, E. V., AYRAPETYAN, S. M. and MATSOYAN, S. G.,
Institute of Organic Chemistry, Armenian Academy of Sciences, Yerevan

[Abstract] Polymerization filling of polyvinyl acetate with foamed perlite sand (100-200 μ m fresh) is studied under aqueous emulsion polymerization conditions without attachment of the initiator to the filler. The experiments produced a uniformly filled polymer when the filler was primed, but if not some PVA was produced which was not bonded to the perlite. Comparatively large volumes of monomer or solvent are required in the process to assure uniform mixing. The quantity of monomer vinyl acetate is determined by the desired composition. Optimal potassium persulfate initiator concentration was 0.01 to 0.02 mol/l. Polymerization filling occurs in 2 to 6 hours with 95 to 100% vinyl acetate conversion. References 3 (Russian).
[133-6508]

COORDINATION OF SCIENTIFIC INVESTIGATION IN LIGNIN CHEMISTRY AND ITS BASIC COMPONENTS

Riga KHIMIYA DREVESINY in Russian No 6, Nov-Dec 82 pp 5-10

KARLIVAN, V. P. and TELYSHEVA, G. M., USSR Academy of Sciences Scientific Council on the Problem "Lignin Chemistry and its Basic Components"

[Abstract] Although preservation of the natural greenery has been a Soviet objective since the founding of the state, little practical realization of this principle came until the 1960s, when rational use of wood products became one of 18 national priority problems. The article surveys state planning and scientific efforts directed toward lignin utilization as a renewable resource as traditional raw materials are gradually exhausted. Attempts are made to use the entire biomass of the forests, to expand the raw material base of the wood processing industries, and to develop pollution-free production technology. Other directions of research include development of bioconversion procedures, biological improvement of hardy ecosystems, biochemical investigations of components of biosynthesis to determine possibilities for directing its influence in growth processes, and physicochemical study of changes in structures and properties of lignin formed under strong anthropogenic influence. Other research is directed toward increasing useful life of wood products, development of new forms of wooden compositions and sheets, producing lignin polymers with increased durability and temperature and corrosion resistance. Agricultural needs from insulation to feeds are also being filled with lignin products. Governmental and research agencies involved in this area are cited.

[98-12131]

CONTRIBUTIONS OF SOVIET LATVIAN SCHOLARS TO DEVELOPMENT OF LIGNIN CHEMISTRY AND CHEMICAL TECHNOLOGY

Riga KHIMIYA DREVESINY in Russian No 6, Nov-Dec 82 pp 11-21

GROMOV, V. S., Institute of Lignin Chemistry, LaSSR Academy of Sciences

[Abstract] This is a review of lignin research and development in Latvia since it became a part of the USSR in 1940, discussing training of personnel and scientific studies under academicians A. Ya. Kalnin'sh, P. N. Odintsov and V. N. Sergeyeva, who worked in the title institute in its earlier forms. Other studies in the Latvian Scientific Research Institute for Forest Product Problems include investigations of furans and related compounds, studies of cell structure, swelling, sorption and lignin reactions with acids, bases and salts. For example, sulfite and alkaline boiling increase internal surfaces and capillary action of fir lignin as cell walls disintegrate, thus changing all physical and chemical properties of the lignin. Other studies have been devoted to hemicellulose changes, submicroscopic structure of lignin, supermolecular structure, the effects of ion radiation on lignin formation of pine and spruce, and numerous related chemical and physical topics. Effects of differential catalysis in consecutive hydrolysis reactions and its importance for pentose formation in a catalytic reaction with sulfuric and acetic acids form the basis for new furfural production technology. Production of vitamin meal, hydroxypropylation of technical lignin to obtain reactive oligoesters, and other products based on extractions from wood are practical aspects that are combined with theoretical and experimental work in the Latvian Institute of Lignin Chemistry. References 30: 29 Russian, 1 Latvian.
[98-12131]

UDC 634.08

ARKHANGELSK, A MAJOR CENTER OF LIGNIN CHEMISTRY IN SOVIET NORTH

Riga KHIMIYA DREVESINY in Russian No 6, Nov-Dec 82 pp 26-31

BOGOMOLOV, B. D., Arkhangelsk Forest Technology Institute

[Abstract] The author reviews activities in the study of chemical properties and supermolecular structural features of lignin and other forest products, and their practical applications, at institutes and production facilities in the city and region of Arkhangelsk, e.g., the Solombalsk Cellulose Paper Plants and the Arkhangelsk Hydrolysis Plants. Educational activities in the area began in 1930 with the establishment of the author's institute. The initial and still important object of theoretical and practical work is wood tar, whose distilling during World War II eventually took the direction of fuel and lubricant production. Various textbooks and monographs came from

scholars at the institute and related "Laboratory for Scientific Problem Solving in the Field of Chemical Processing of Lignin and Utilization of Waste Products from Paper and Hydrolytic Production" and the academic "Department of Lignin, Cellulose and Hydrolytic Chemistry." The Lignin Laboratory of the All-Union Scientific Production Association for Paper Production is another leading organization for research in lignin chemistry and technology, concentrating on use of sulfate, thallol, lignin silt, lignosulfonate and tar by-products of wood manufacture for wood fiberboards, cardboards and wrapping papers. References 11 (Russian).
[98-12131]

UDC 676

CONTRIBUTIONS OF UKRAINIAN SCIENTIFIC RESEARCH INSTITUTE FOR PAPER AND PULP PRODUCTION

Riga KHIMIYA DREVESINY in Russian No 6, Nov-Dec 82 pp 32-37

GRITSULYAK, V. N. and ZAPLATIN, V. P., Ukrainian Scientific Production Association for Paper Production

[Abstract] This is a review of the history of paper production in the Ukraine from prerevolutionary times to the present. The title institute was founded as a branch of its all-union counterpart in 1931, and became an independent research center in 1955. Prior to World War II it had developed a monosulfite-sulfate procedure for boiling straw cellulose to regenerate 70-75% of the processed lye, while using wastes of the Rubezhansk phenol plant in the process. Local raw materials such as flax straw and other products of agriculture were also put to productive use. An important research and development project resulted in production of paper for aluminum oxide condensers for various electronic applications in the late 1970s. Foliage of beech, birch, alder and aspen has been put to use in cardboard manufacture through the institute's research. Other products developed by the institute include chalk-coated papers, anticorrosive papers and condenser insulations, natural sorbents for purifying sewage in condenser paper production, and various solutions to problems of pollution in the paper and pulp industries. Recently the institute has turned its attention in the direction of automation processes for these industries.
[98-12131]

SIBERIAN ORDER OF LABOR RED BANNER TECHNOLOGICAL INSTITUTE, CENTER OF
LIGNIN CHEMISTRY RESEARCH IN SIBERIA

Riga KHIMIYA DREVESINY in Russian No 6, Nov-Dec 82 pp 38-42

LEVIN, E. D., Siberian Technological Institute

[Abstract] Since its establishment as the Krasnoyarsk Wood Technology Institute in 1952, the title institute has directed its efforts at such topics as processes in wood tissues (under Professor E. D. Levin), learning new facts about the annual cycles in the cambial zone and bast of larch that effect content of acylglycerol and free fatty acids, and research and development of technology for using foliage of trees native to Siberia (under the direction of Associate Professor S. M. Repyakh). The latter research has determined that ester oils and their fractions, such as monoterpenes, sesquiterpenes, high-boiling-point types and oxygen-containing fractions have pronounced antimicrobial activity with low toxicity for other life. A third direction is research and development of technology by larch by-product hydrocarbons: other areas of research are development of theoretical and practical aspects of larch utilization in paper and pulp production, including mathematical models for automated production systems, study of the role of morphological and anatomical aspects of cell walls in delignification and fiber production, both from the point of view of hydrodynamic methodology and features of durability of such cellulose fibers, and study of sorption properties of hydrolyzed lignin for precipitation of photographic silver from used developing solutions. Thallol production to obtain products for household chemicals is another area of research.

[98-12131]

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